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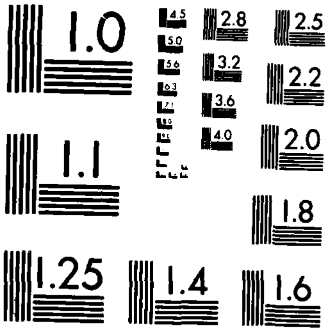

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The Effect of Electric Field on The Free Energy of $SbS_{1-x}O_xI$

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Calculation of free-energy coefficients for ferroelectrics having axial polarization is performed for two conditions: i.e., with and without an electric field. An experiment to evaluate these coefficients for $SbS_{1-x}O_xI$ versus temperature and pressure is described. The results are displayed as shifts in the Curie temperature and pressure as a function of electric field and are found to be in good agreement with phenomenological theory predictions.

CONTENTS

THE EFFECT OF ELECTRIC FIELD ON THE FREE ENERGY OF $SbS_{1-x}O_xI$

I. INTRODUCTION

The knowledge of the Gibbs free-energy coefficients is necessary when one attempts to determine the thermodynamic properties of a material. This has been demonstrated by Devonshire [1,2] and later by Jona and Shirane [3] for ferroelectric materials. An interesting feature of Jona and Shirane's derivation is that the free-energy coefficients may be determined by several methods. One can measure the dielectric constant and polarization along the c-axis versus temperature in a range about the Curie point or monitor just the dielectric constant versus temperature as a function of direct-current (dc) electric fields. Both methods yield the coefficients of the ferroelectric terms of the free energy and suggest an interesting way to test the consistency of the experiments. Another salient feature of the electric-field method is that it can also be used to determine the phase transition order (3).

The comparison looks even more enticing when applied to alloys. The basic Devonshire approach has been extended by the author to $SbS_{1-x}O_xI$ alloys [4-6], $SbSI_{1-x}Br_x$, and on $PbZr_xTi_{1-x}O_3$ alloys [7]. Several authors [8,9] have investigated the influence of a dc electric field on the shift of the Curie temperature of pure SbSI, but no similar attempt to find the shift of the Curie pressure has been reported.

The purpose of this article is to present an approach to $SbS_{1-x}O_xI$ using an electric field. The free-energy coefficients of $SbS_{1-x}O_xI$ alloys determined by using both methods may be compared in order to verify their equivalence and contribute to the state of knowledge on $SbS_{1-x}O_xI$ alloys. In Section II the necessary relations are developed to solve for the free energy of an alloy via field-dependent dielectric constant measurements. In Section III the experiment is described; i.e., the measurements of dielectric constant versus temperature and pressure under the applied dc electric field. The experimental results are also given in that section. The comparison and the discussion of the results conclude the work in Section IV.

II. THEORY

The Gibbs free energy of a crystal having an axial polarization (such as $BaTiO_3$, SbSI, etc.) is:

$$A_i = \alpha_i P_{i,3}^2 + \beta_i P_{i,3}^4 + \gamma_i P_{i,3}^6 , \tag{1}$$

where all the coefficients are temperature dependent and $P_{i,3}$ is the polarization along the c-axis. The index i denotes the parents of the binary alloy (i = 1,2) or the alloy itself (i = 0). The alloy is assumed to have the same symmetry as its parents [4-7]. The coefficients α_o, β_o, γ_o will be, therefore, concentration-dependent.

Assuming the following properly weighted relation among the free energy of the alloy and those of the parents, one can proceed to calculate the relations among all the coefficients involved:

$$A_o = A_1 x + A_2(1 - x) + A_3 x(1 - x) \ . \tag{2}$$

Here x is the concentration of the hypothetical oxygen parent (SbOI), and A_3 is a quadratic interaction term. One can assume next [4-7] the following explicit form for A_3:

$$A_3 = \alpha_3 P_{1,3} P_{2,3} + \beta_3 P_{1,3}^2 P_{2,3}^2 + \frac{1}{2}\gamma_3 (P_{1,3}^2 P_{2,3}^4 + P_{1,3}^4 P_{2,3}^2), \tag{3}$$

in which α_3, β_3, and γ_3 are the coefficients of a quadratic interpolation energy. One further assumes [4-7] that $\vec{P}_1 = \vec{P}_2 = \vec{P}_0$, which yield the coveted relations among all the coefficients:

$$\alpha_0 = \alpha_1 x + \alpha_2(1 - x) + \alpha_3 x(1 - x) \tag{4a}$$

$$\beta_0 = \beta_1 x + \beta_2(1 - x) + \beta_3 x(1 - x) \tag{4b}$$

$$\gamma_0 = \gamma_1 x + \gamma_2(1 - x) + \gamma_3 x(1 - x) \ . \tag{4c}$$

As discussed in References 4-7, two options to determine the coefficients α_0, β_0, and γ_0 come to mind immediately:

a. Deduce α_0, β_0, and γ_0 directly from measurement to which the alloy is subjected directly.

b. Calculate the coefficients of the other alloys from the interpolation constants. This, however, requires the complete knowledge of the parents and one alloy in order to calculate the characteristics of all other alloys.

In both cases the necessary measurements, as derived from Devonshire theory, are shown in Table 1a and the assumption is made that out of all the discussed coefficients, only the α_i's depend on temperature [3] and are in the regular Curie-Weiss form:

$$\alpha_i = \frac{4\pi}{C_i}(T - T_{0,i}) \tag{5a}$$

$$\tilde{\alpha}_i = \frac{4\pi}{C_i} \tag{5b}$$

where C_i and $T_{0,i}$ are the Curie constant and the Curie-Weiss temperature of the constituent i.

Jona and Shirane [3] considered also a different approach that leans heavily on the effects of electric field on the dielectric constant. While α_i is determined from Eq. (5) in the familiar routine (see Table 1a), β_i and γ_i are determined from the following relations:

$$\varepsilon_{i,33}^{E}(T) - \varepsilon_{i,33}^{0}(T) = -\frac{12[\varepsilon_{i,33}^{0}(T)]^4 \beta_i}{(4\pi)^3 E^2} \tag{6}$$

$$\frac{dT_{c,i}}{dE} = \frac{C_i}{4\pi}\left(-\frac{2\gamma_i}{\beta_i}\right)^{1/2} . \tag{7}$$

Here $\varepsilon_{i}{}^{E}_{i,33}(T)$ is the dielectric constant at a nonvanishing dc electric field E while $\varepsilon_{i}{}^{0}_{i,33}(T)$ is its value for $E = 0$, both for the i^th constituent and the c-axis. The corresponding gradient of the Curie temperature with electric field is $dT_{c,i}/dE$. Equations (5) through (7) are sufficient to determine α_i, β_i, and γ_i and are summarized in Table 1b. A bonus originating from Eq. (7)

Table 1a. The free-energy coefficients and the corresponding measurements required ($i = 0, 1, 2$)

Measurements with no electric field for both first- and second-order transitions.

	First Order		Second Order	
Coefficient	Expression	Measurements	Expression	Measurements
$\tilde{\alpha}_i^{*}$	$4\pi/c_i$	$\varepsilon_{i,33}$ vs. T @ $T>T_c$	$4\pi/C_i$	$\varepsilon_{i,33}$ vs. T @ $T>T_c$
β_i^{**}	$-8\pi/(\varepsilon_{i,33}P_{i,3}^{2})$	$\varepsilon_{i,33}, P_{i,3}$ @ $T = T_c$	$\pi/(2\varepsilon_{i,33}P_{i,3}^{2})$	$\varepsilon_{i,33}, P_{i,3}$ @ $T<T_c$
γ_i	$4\pi/(\varepsilon_{i,33}P_{i,3}^{4})$	$\varepsilon_{i,33}, P_{i,3}$ @ $T = T_c$	--	--

*$\tilde{\alpha}_i$ is found from α from Eq. (S-2). The measurement of $\varepsilon_{i,33}$ vs. T provides also for T_o.

**Values for this coefficient are given at some arbitrary temperature T_r for the second-order case. Normally T_r is chosen as the room temperature (25°C) but in this case, was 20°C below T_o.

Table 1b. The free-energy coefficients and the corresponding measurements required ($i = 0, 1, 2$)

Measurements with electric field for first-order transition

Coefficient	Expression	Measurements
$\tilde{\alpha}_i$	$4\pi/C_i$	$\varepsilon^{0}_{i,33}$ vs. T @ $T>T_c$
β_i	$\dfrac{(4\pi)^3E^2[\varepsilon^{0}_{i,33}(T) - \varepsilon^{E}_{i,33}(T)]}{12\ [\varepsilon^{0}_{i,33}(T)]^4}$	$\varepsilon^{E}_{i,33}$ and $\varepsilon^{0}_{i,33}$ at any T vs. small E values.
γ_i	$\dfrac{(4\pi)^5E^2}{24C_i}\ {\dfrac{dT_{c,i}}{dE}}^{2}\ \dfrac{\varepsilon^{E}_{i,33}(T) - \varepsilon^{0}_{i,33}(T)}{[\varepsilon^{0}_{i,33}(T)]^4}$	$\varepsilon^{E}_{i,33}$ and $\varepsilon^{0}_{i,33}$ vs. T at small fields.

is the potential to determine the order of the transition. While γ_i is considered always positive, β_i is negative for a first-order transition and positive for a second-order one. A change in the sign of $dT_{c,i}/dE$ means a second-order transition. As this quantity approaches zero, it denotes a tricritical point. One should bear in mind that Eq. (7) is correct only for first-order transitions, and another expression should be worked out for the second order [3].

When Eqs. (6) and (7) are written for an alloy using Eqs. (4) to determine the interpolation constants, one gets:

$$\varepsilon^{E}_{i,33}(T) - \varepsilon^{0}_{i,33}(T) = \frac{12[\varepsilon^{0}_{i,33}(T)]^{4}}{4\pi^{3}E}\,[\beta_1 x + \beta_2(1 - x) + \beta_3 x(1 - x)] \tag{8}$$

and

$$\frac{dT_{c,i}}{dE} = \frac{2^{1/2}C_i}{4\pi}\,\left[-\,\frac{\gamma_1 x + \gamma_2(1 - x) + \gamma_3 x(1 - x)}{\beta_1 x + \beta_2(1 - x) + \beta_3 x(1 - x)}\right]^{1/2} . \tag{9}$$

As one can clearly envisage, Eqs. (6) and (7) are typical of attaining α_0, β_0, and γ_0 from measurements while Eqs. (8) and (9) allow one to calculate the coefficients of other alloys.

The extension of the above-mentioned considerations to include nonvanishing pressures is straightforward when one incorporates the Samara [10] transformation into the development. The pressure-dependent coefficients are starred. It follows from the former assumptions [4] that:

$$\beta_i^{*} = \beta_i \tag{10}$$

$$\gamma_i^* = \gamma_i \ , \tag{11}$$

while

$$\alpha_i^* = \frac{4\pi}{C_i^*}(p - p_{o,i}^*) \tag{12a}$$

$$\tilde{\alpha}_i^* = \frac{4\pi}{C_i^*} \ , \tag{12b}$$

where

$$p - p_{o,i}^* = (T - T_{o,i})/(dT_{o,i}/dp) \tag{13}$$

$$C_i^* = C_i/(dT_{o,i}/dp) \ . \tag{14}$$

Here C_i and $p_{o,i}$ are the Curie constant for nonvanishing pressures and the Curie-Weiss pressure. As implied by Eqs. (13) and (14), they are derived from their zero-pressure counterparts through division by the Ehrenfest temperature gradient.

The derivation of expressions analogous to Eqs. (4), (8), and (9) is straightforward and will not be included.

III. EXPERIMENT AND RESULTS.

A two-fold experiment was conducted that:

a. determined the polarization and dielectric constant as a function of temperature and pressure,

b. measured the dielectric constant in the presence of an electric dc bias field as a function of temperature and pressure.

The first part of this experiment has already been described elsewhere [4,5] and will not be presented in detail here.

The samples used in both experiments were grown by the Material Research Laboratory of the Pennsylvania State University. They were received as 9-mm to 12-mm diams and up to 25-mm long. Samples were cut using a diamond saw and polished to #600 before electroding. To increase their mechanical strength, they were impregnated in SPURR's low-viscosity epoxy under vacuum. Then the final samples were reshaped to their original diameter with the typical final thickness between 2 mm and 6 mm. Dynalloy 350 fast-curing silver paint was used for the electrodes. All samples were polarized at 1.5-kV/cm at -11°C.

The dielectric constant was measured by a General Radio 1683 automatic RLC bridge at 1 kHz. The samples were immersed in castor oil. Temperature was controlled between -12 and +60°C, and pressures to 100 MPa were obtained using a pressure pump and a BLH 1200 digital strain indicator. A dc field was applied by a filtered power supply.

The concentrations of the oxygen parent used (in molar percents) were 0, 4, 8, 12, and 20. As the samples were highly conducting near their Curie temperature, even fields of 10 V/cm could cause breakdown. Although such fields are by no means extreme, some breakdowns did occur. This prevented comparison with the results of option a in Section II of the experiment for x = 4, 8, and 20%. The data finally used were measurements on pure SbSI, $SbS_{0.92}O_{0.08}I$, and $SbS_{0.88}O_{0.12}I$ to compare the Curie temperature and pressure shifts and the free-energy coefficients. The data were plotted as the Curie temperature and pressure versus field in Figs. 1 and 2. Figure 3 is an example of the actual $1/\varepsilon_{i,33}$ measurements as a function of E. Linear regressions of $1/\varepsilon_{i,33}$ versus T (or p) were calculated (see Fig. 3) both for the last three points below $T_{c,i}$ and for all of those above $T_{c,i}$. The straight lines obtained were then intersected to find the Curie temperature (or pressure) at the relevant field.

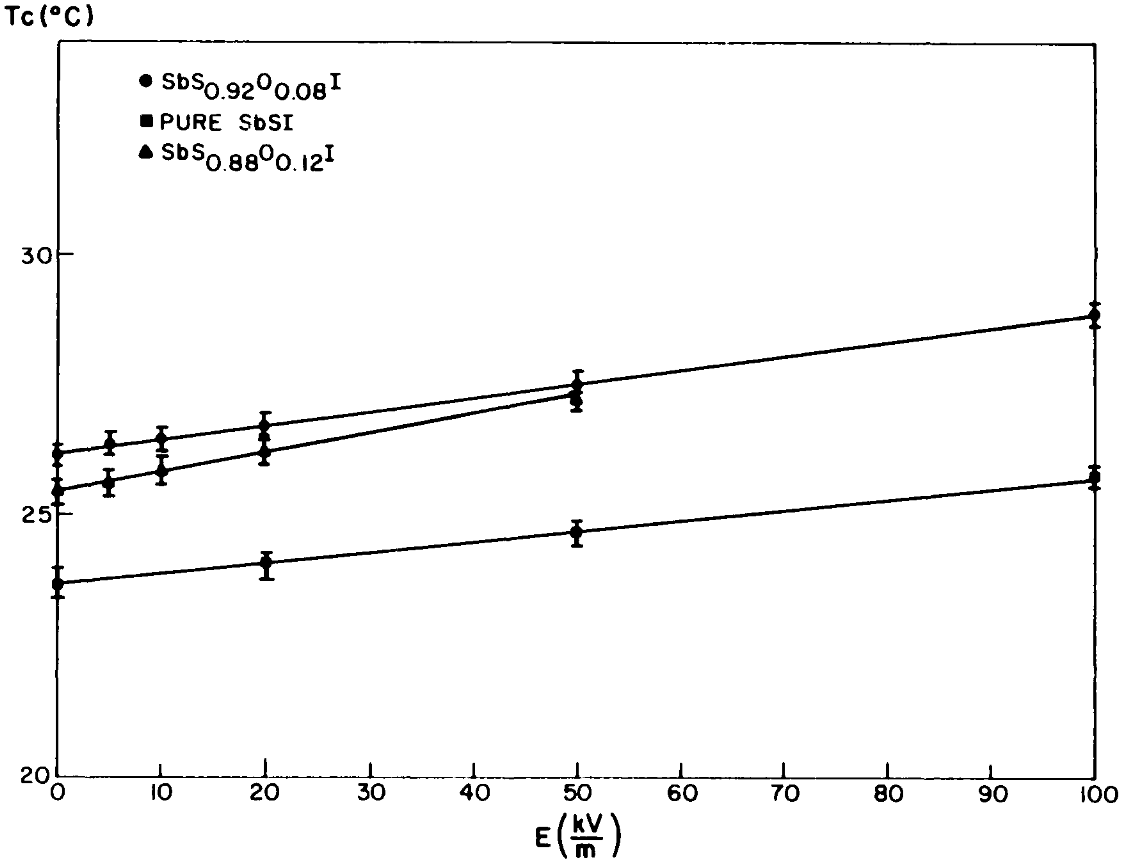

Fig. 1 - Curie temperatures for various $SbS_{1-x}O_xI$ alloys as functions of a dielectric constant electric field

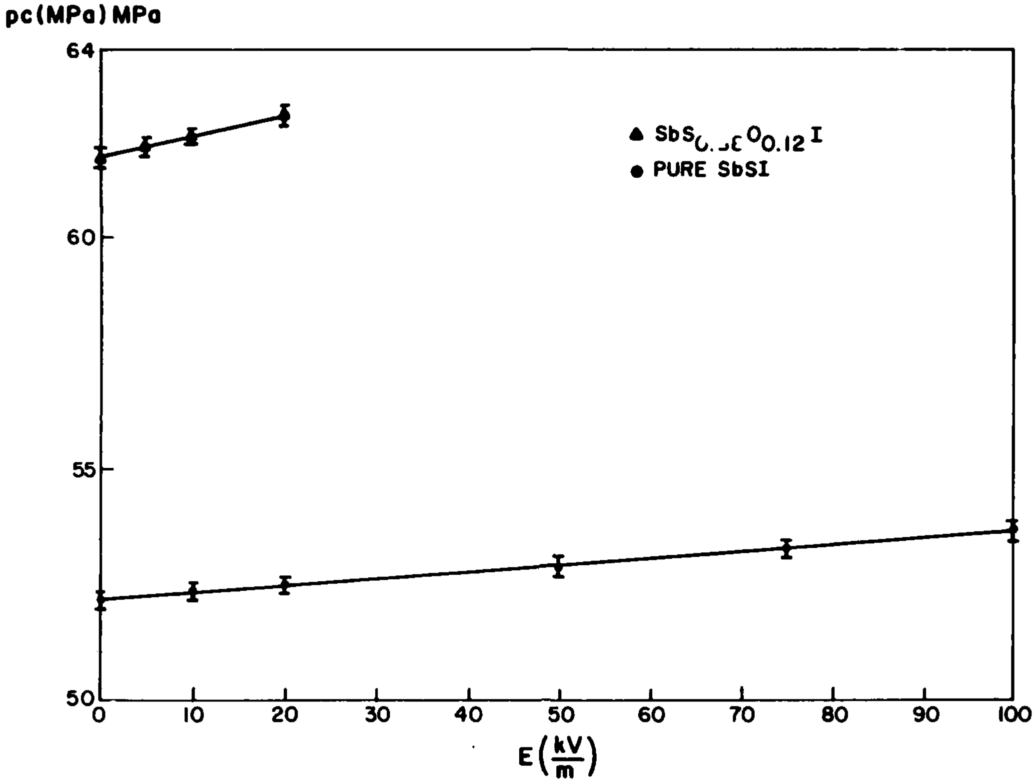

Fig. 2 - Curie pressures for various $SbS_{1-x}O_xI$ alloys as functions of a dielectric constant electric field

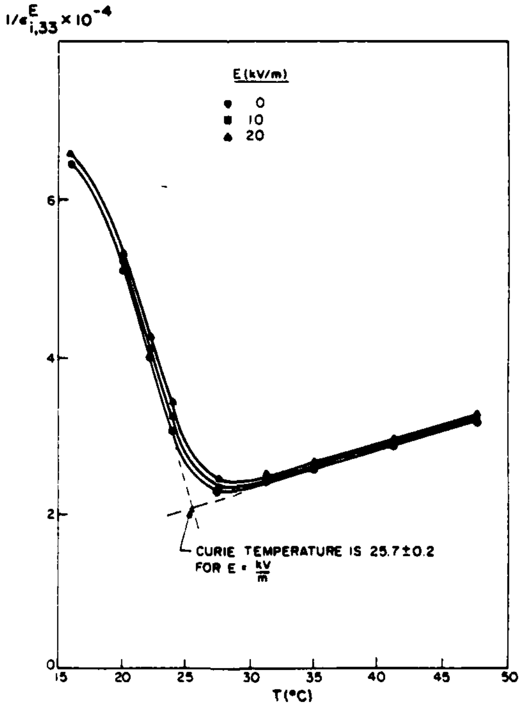

Fig. 3 - Reciprocal dielectric constant vs temperature at various dielectric constant fields for $SbS_{0.88}O_{0.12}I$

IV. DISCUSSION

It is interesting to note that $T_{c,i}$ changes linearly with E (see Figs. 1 and 2) as predicted by Eq. (9) for each concentration. The values for $dT_{c,i}/dE$ are also in fair agreement with those of Toyoda et al. [9]. It is worthwhile to examine the dependence of the Curie temperature gradient with pressure on the electric field. One may use the mathematical identity:

$$\left(\frac{\partial T_{c,i}}{\partial E}\right)_p \left(\frac{\partial E}{\partial p_{c,i}}\right)_T \left(\frac{\partial p_{c,i}}{\partial T_{c,i}}\right)_E = -1 \qquad (15)$$

to examine this dependence. This test, when applied to small dc electric fields, can check the consistency of the experimental method: The $[(dT_{c,i})/(\partial p_{c,i})]_E$ values are:

7.9 ± 2.0°C/GPa for pure SbSI
-4.3 ± 1.0°C/GPa for $SbS_{0.92}O_{0.08}I$
-7.7 ± 2.0°C/GPa for $SbS_{0.88}O_{0.12}I$.

The value for pure SbSI is in fair agreement with the result of -4.7 ± 2°C/GPa quoted by Samara [11] for epoxy-bonded samples.

The gradients of the Curie temperatures and pressures with electric field for each alloy are summarized in Fig. 4 in two frames. The gradients of the Curie tempertures and pressures are plotted as a function of oxygen concentration in the alloy. The data presented in Section III are plotted as crosses and should be compared to the values calculated from Eq. (7) which are

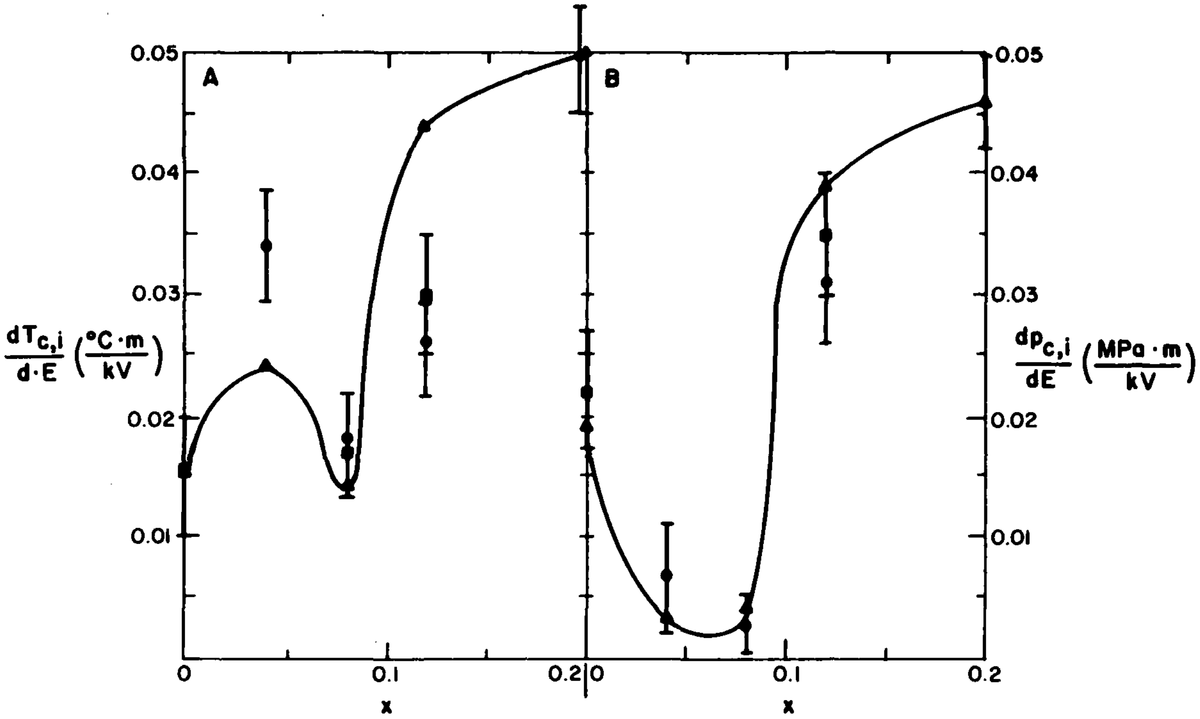

Fig. 4 - Gradients of the Curie temperatures (A) and pressures (B) as functions of the oxygen concentration in $SbS_{1-x}O_xI$. Crosses are direct measurements (see Section III), full circles are values calculated from Eq. (7) using the free-energy coefficients at zero field for each sample. The curve represents the result of the interpolation scheme [see Eq. (9)] when applied to the range $0 \leq x \leq 0.2$.

displayed as full circles. The solid curve joining the triangles represents the dependency predicted by the interpolation scheme of Eq. (9) when applied to the range $0 \leq x \leq 0.2$. Due to the shortage of experimental data with field, it is difficult to test the validity of the interpolation method when applied to the field-oriented results. One can carefully state, though, that the interpolation method will deliver results of the same quality regardless of the presence of field. This is corroborated by the proximity of the experimental points obtained by both methods (see again Fig. 4).

It looks in Fig. (4) as if the minimum in the values of both $dT_{c,i}/dE$ and $dp_{c,i}/dE$ may indicate that the alloy system possesses a tricritical point phase transition. However, the evidence is only circumstantial at this time. It is noted that in Fig. 4a a minimum appeared at $x = 0.08$, whereas for $x = 0.04$ the alloy $SbS_{0.96}O_{0.04}I$ exhibited the largest $T_{c,i}$ and $p_{c,i}$ [4]. This situatin may be coincidental. The magnitude of $T_{c,i}$ and $p_{c,i}$ depends on the α_i coefficient of the free energy (Eqs. 5 and 12), and $dT_{c,i}/dE$ and $dp_{c,i}/dE$ upon β_i and γ_i coefficients [Eqs. (1) and (7)]. Therefore, one cannot correlate the peak in $T_{c,i}$ and $p_{c,i}$ with the valley in $dT_{c,i}/dE$ and $dp_{c,i}/dE$, respectively.

The high conductivity of $SbS_{1-x}O_xI$ close to the transition point proved to be detrimental to some of the samples used. The conductivity depends, to a certain extent, on the growth technique and the choice of the raw materials. Some of the points raised in this discussion could have been better examined had the samples been less conductive.

One should consider now the material problems contributing to the observed errors. The orientation of the samples is not perfect since they were grown by using the Bridgman method. Some spread in results is expected because of the misalignment, and one can expect this spread to broaden if the growth mechanism is affected by the addition of various oxygen quantities. While the pure SbSI and the $SbS_{0.8}O_{0.2}I$ samples are highly aligned, $SbS_{0.92}O_{0.08}I$ and $SbS_{0.88}O_{0.12}I$ are less well oriented. A sample of $SbS_{0.96}O_{0.04}I$ has also been tested, but the results were not presented due to the mediocre orientation. The criterion for presenting the results was that the worst misorienttion ot needles would be less than 35°.

One should also consider the instrumentation precision. The accuracy of the capacitance bridge is better than 0.1%, and the field calibration was accurate to within 2%. In spite of these, it was felt that the accuracy of the transition point is less (mainly due to the ±0.2°C inaccuracy in the temperature and ±0.01 MPa in the pressure readings). The transition, although of first order [12], is smeared. The considerable slope of the reciprocal dielectric constant with temperature (or pressure) contributes to the accumulated error. The accuracy of the measurement was, therefore, secondary in nature to this effect and was considered adequate for the purpose of this work.

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