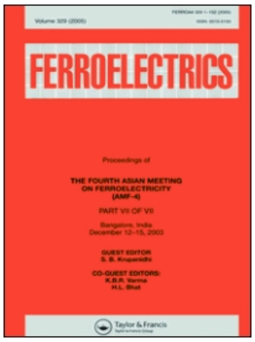

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Temperature and pressure dependence of the Raman intensity and frequency of a soft mode near the tricritical point in the ferroelectric SbSI

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ABSTRACT
We analyze the pressure dependence of the intensity and the frequency of a soft mode from the Raman and elastic light scattering experiments as reported in the literature close to the ferroelectric – paraelectric transition in SbSI crystal. The Raman intensity of this mode is analyzed as a function of pressure at constant temperatures of 272 K (first order transition) and 234 K (tricritical or second order transition) according to a power-law formula. Our analysis of the Raman intensity gives closely the mean field values for the order parameter. From our analysis, we also obtain that the Raman frequency (squared) of the soft mode varies linearly with the pressure at constant temperatures close to the ferroelectric - paraelectric transition in SbSI as obtained experimentally.

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KEYWORDS
Raman intensity and frequency; soft mode; tricritical point; ferroelectric SbSI

1. Introduction

SbSI is a semiconductor with a band gap near 6200 Å. The ferroelectric phase occurs in this material at ∼293 K at atmospheric pressure. This transition is of a first order type (discontinuous at the transition temperature T_c). At a temperature of 234 K and 1.5 kbar pressure, a first order transition changes toward a second order (continuous at T_c) and, the phase lines of the first order and second order transition coincide at the tricritical point [1]. So, the tricritical behavior in SbSI exhibits both the first order (discontinuous) and second order (continuous) features.

The existence of the tricritical point in antimony sulpho-iodide (SbSI) was studied experimentally by the early measurements of the pressure dependence of inverse dielectric permittivity [2] and the forbidden bandwidth with the temperature dependence of the crystal length has been measured recently [3].

As reported some years ago, the band gap strongly depends on the electric field [4] and it varies with temperature [5] in the antimony sulfo-iodide (SbSI) which exhibits both photoconductive and ferroelectric properties [6, 7] as the first semiconductor.

SbSI crystals undergo three phases, namely, ferroelectric $P_{na21}(C_{2v}^{9})$ phase below 298 K (T_c = 295 K) antiferroelectric phase in the temperature interval of 298 to 410 K and

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paraelectric $P_{nam}(D_{2h}^{16})$ phase above 410 K [8, 9]. At around $T_c = 410$ K, a small anomaly of thermal expansion and microwave permittivity occurs [9].

In regard to the tricritical point that occurs in the SbSI crystal as stated above, it has been reported [3] that the coexisting phase structure near the first-order phase transition decreases with pressure and that it becomes zero at the tricritical point (TCP). It has been observed experimentally in the Raman spectra that the intensity and the frequency of the soft mode change considerably above the critical pressure P_c and below the critical temperature T_c in SbSI [1]. From the Raman experiments, it was observed that an optical $\Gamma_1(A_1)$ band which consists of two optical modes, exhibits a soft-mode behavior close to T_c with increasing temperature from the ferroelectric phase [10]. Also, from the infrared reflectivity measurements, the optical mode is the temperature dependent with decreasing temperature from the paraelectric phase in SbSI [11], as stated previously [12]. The soft mode coupling with the 30 cm^{-1} mode [13] and, the coupling between the 48 cm^{-1} and 41 cm^{-1} modes have been observed for the pressure induced phase transition in SbSI [12]. It has been stated that under the influence of the anharmonicity, the soft mode splits [14] and different compounds of the soft mode appear in IR and millimeter wave spectra. The anharmonicity of the soft mode has been studied from the dependence of the potential energy of those modes on the normal coordinates through the interaction of phonons [15, 16] and the electron-phonon interaction [17, 18].

In this study, we analyze the experimental measurements for the Raman intensity as a function of pressure at two constant temperatures of 272 K and 234.2 K for the pressure-induced phase transition in SbSI [1]. The ferroelectric – paraelectric transition is investigated away from (272 K) and close to the tricritical point (234.2 K) in this ferroelectric material.

This analysis of the Raman intensity of the soft mode at various pressures (272 K and 234.2 K) is conducted using a power-law formula with the critical exponent φ' ($P < P_c$ in the ferroelectric phase) and φ ($P > P_c$ in the paraelectric phase) for the order parameter in SbSI. We also analyze here the pressure dependence of the Raman frequencies of this soft mode at constant temperatures (241, 231, 202, 150 and 119 K) using the experimental data [1] in SbSI. A linear variation of the Raman frequency (squared) for the soft mode with the $P_c - P$ is constructed, as observed experimentally [1] in SbSI.

Below, in sections 2 and 3, we give our analyses of the Raman intensity and the frequency for the soft mode, respectively. In section 4, we discuss our results. Conclusions are given in section 5.

2. Analysis of the Raman intensity

Experimental data [1] for the Raman intensity *I(0)* as a function of pressure using the Raman and elastic light scattering (Rayleigh) at constant temperatures of 272 K and 234.2 K were analyzed.

This analysis was performed according to a power-law formula.

$$I\ (0)\ =\ I_0(P\ -\ P_c)^{2\varphi} \tag{1}$$

for the paraelectric phase (PE) above P_c and

$$I\ (0)\ =\ I_0{}'(P_c\ -\ P)^{2\varphi'} \tag{2}$$

for the ferroelectric phase (FE) below P_c.

Table 1. Values of the critical exponent φ' and the intensity I_0' for the ferroelectric (FE) phase of SbSI within the pressure intervals indicated according to Eq. (2). Values of the critical pressure P_c are also given.

T (K)	φ'	I_0'	P_c(kbar)	Pressure Interval(kbar)
272	0.18	0.382	0.462	$0.390 < P < 0.461$
234.2	0.20	2.227	1.399	$1.322 < P < 1.396$

In Eqs. (1) and (2), P_c is the critical pressure, φ' or $'$ is the critical exponent for the order parameter and I_0 (or I_0') is the amplitude.

By taking the logarithms of both Eqs. (1) and (2), we get

$$ln\ I(0) = ln\ I_0 + 2\ \varphi\ ln\ (P - P_c) \tag{3}$$

and

$$ln\ I(0) = ln\ I_0^{'} + 2\varphi^{'} ln\ (P_c - P) \tag{4}$$

Table 1 gives the values of the fitted parameters $\varphi'$and I_0' in the FE phase of SbSI according to Eq. (2).

Similarly, Table 2 gives the values of the fitted parameters φ and I_0 in the PE phase of SbSI according to Eq. (1).

Figure 1 gives the variation of $I(0)$ with the $(P_c - P)$ in a log-log scale for the ferroelectric (FE) phase in SbSI at 272 K according to Eq. (4).

We give in Fig. 2 a log-log plot of $I(0)$ against $(P - P_c)$ for the paraelectric (PE) phase in SbSI at 272 K according to Eq. (3).

Since Eq. (3) gives us a straight line, we divided our plot into the two pressure intervals, as shown in Figure 3.

Finally, we plot $ln\ I(0)$ against $(P_c - P)$ for a constant temperature of 234.2 K close to the tricritical point (T = 235 K, P = 1.5 kbar) in the FE phase of SbSI as given in Fig. 4. according to Eq. (4). For the paraelectric (PE) phase, our plot is given in Fig. 5 (Eq. 3).

3. Analysis of the Raman frequency

In this part, we analyzed the experimental data [1] for the Raman frequencies of the soft mode associated with the transition between the ferroelectric and paraelectric phases in SbSI. This analysis was performed for the pressure dependence of the Raman frequency according to

$$w^2 = a\ (P_c - P)\ +\ b \tag{5}$$

where a and b are constants. P_c denotes the critical pressure. We analyzed the Raman frequencies of the soft mode, which were measured as a function of pressure at constant

Table 2. Values of the critical exponent φ and the intensity I_0 for the paraelectric (PE) phase of SbSI within the pressure intervals according to Eq. (1). Values of the critical pressure P_c are also given.

T(K)	φ	I_0	P_c(kbar)	Pressure Interval (kbar)
272	0.56	1.03	0.462	$0.465 < P < 0.477$
	0.15	2.27	0.462	$0.477 < P < 0.501$
234.2	0.32	4.96	1.399	$1.401 < P < 1.459$

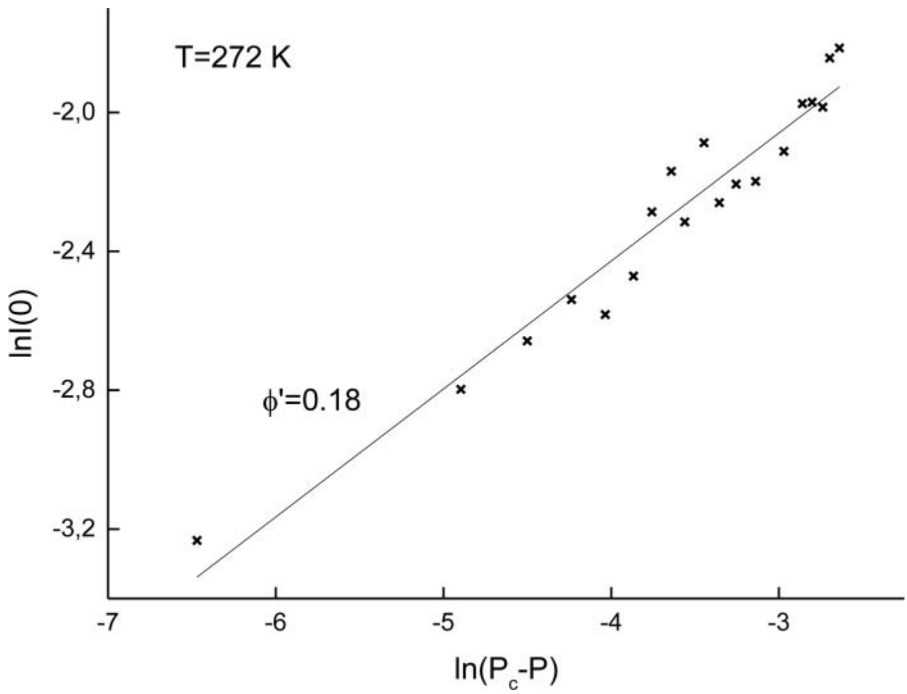

Figure 1. The Raman intensity of the soft mode as a function of $P_c - P$ in a log-log scale for a constant temperature indicated according to Eq. (4) within the pressure interval (Table 1) in the ferroelectric phase of SbSI.

temperatures [1]. From the linear fits of w^2 vs. P according to Eq. (5), we extracted the values of the coefficients a and b within the pressure intervals, as given in Table 3.

4. Discussion

In the first part of this study, we analyzed the pressure dependence of the Raman intensity, *I(0)* for the soft mode at the two constant temperatures of 272 and 234.2 K, as plotted in a log-log scale in Figs. (1–5) for SbSI. As stated above, this soft mode is associated with the ferroelectric – paraelectric phase transition in SbSI. This transition becomes a tricritical one (both discontinuous and continuous transitions) at $T_c = 234.3$ K ($P_c \approx 1.4$ kbar) for SbSI, as observed experimentally [1].

At a constant temperature of T = 272 K, there is a discontinuous change in the Raman intensity I(0) of the soft mode, which decreases with decreasing pressure toward the critical pressure P_c from the paraelectric phase of SbSI, as observed experimentally [1]. This decrease in the Raman intensity is due to the order parameter fluctuations near P_c, as also stated previously [1]. Below P_c in the ferroelectric phase the Raman intensity *I(0)* increases as the pressure decreases, which is associated with the increasing domain size [1]. With this discontinuous change in the Raman intensity *I(0)* at P_c for T = 272 K, the hysteresis effects appear [1].

At a constant temperature of $T \approx 234$ K, there occurs a continuous change in the Raman intensity *I(0)* of the soft mode with decreasing pressure toward the P_c from the paraelectric

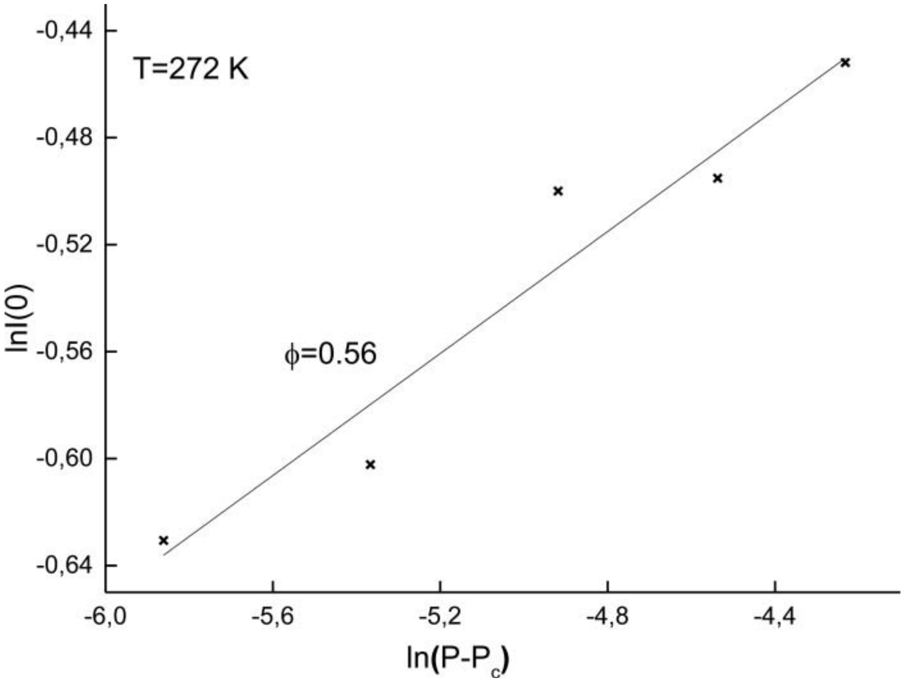

Figure 2. The Raman intensity of the soft mode as a function of $P - P_c$ in a log-log scale for a constant temperature indicated according to Eq. (3) within the pressure intervals (Table 2) in the paraelectric phase of SbSI.

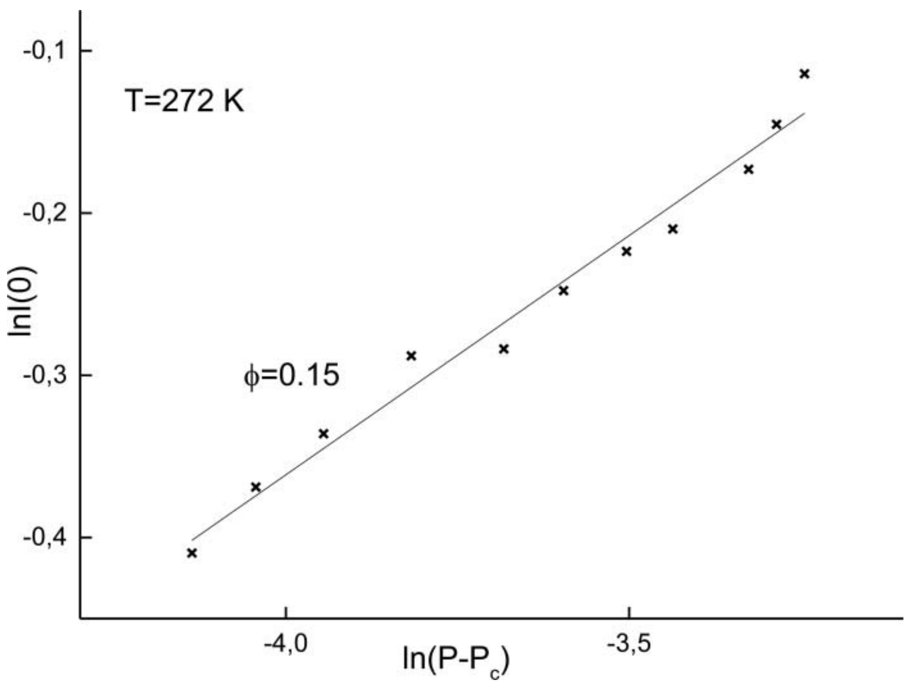

Figure 3. The Raman intensity of the soft mode as a function of $P - P_c$ in a log-log scale for a constant temperature indicated according to Eq. (3) within the pressure intervals (Table 2) in the paraelectric phase of SbSI.

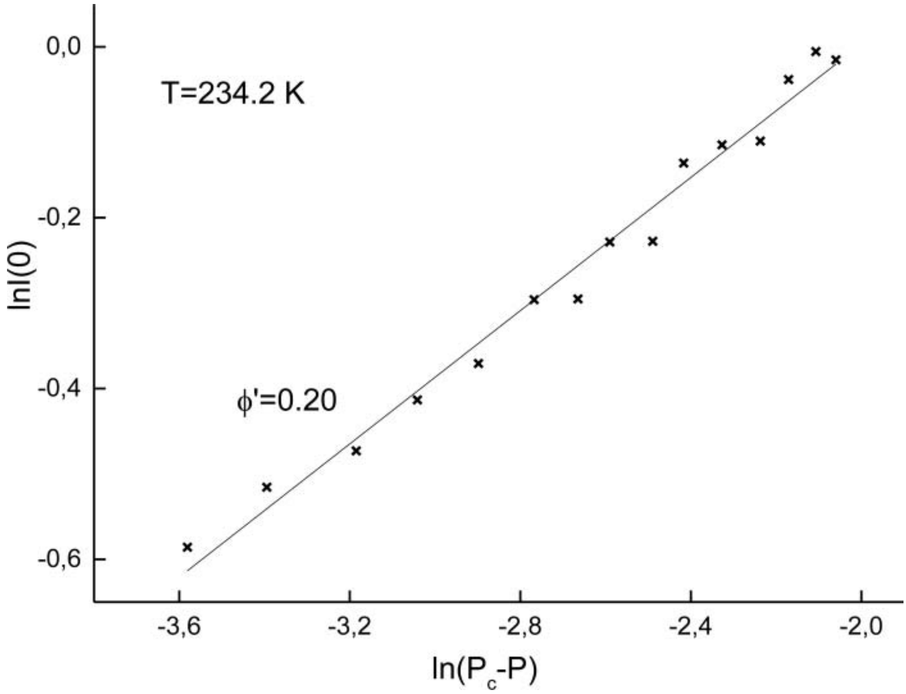

Figure 4. The Raman intensity of the soft mode as a function of $P_c - P$ in a log-log scale for a constant temperature indicated according to Eq. (4) within the pressure interval (Table 1) in the ferroelectric phase of SbSI.

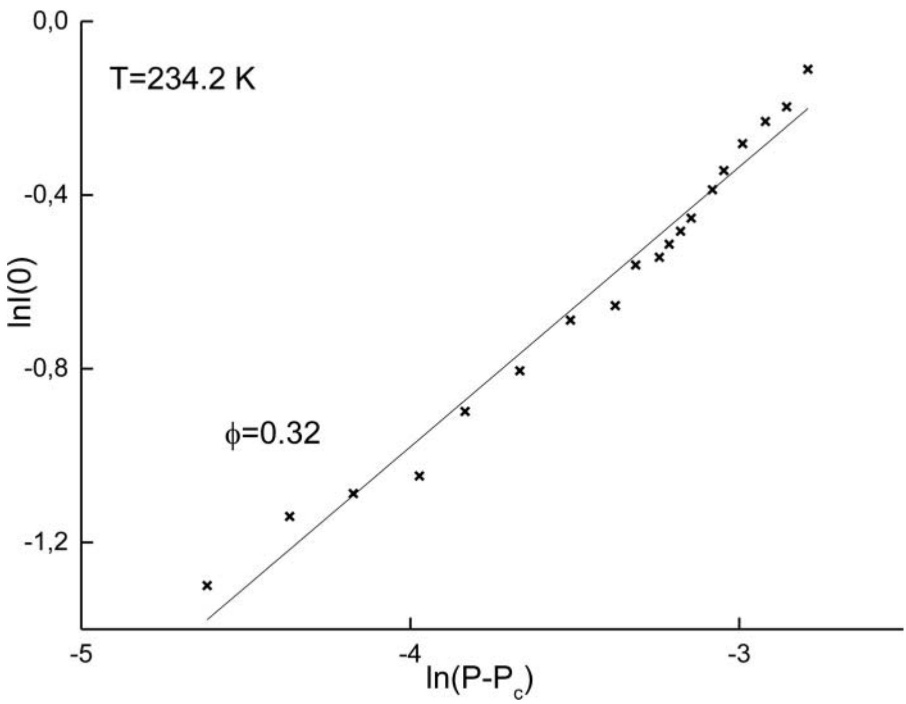

Figure 5. The Raman intensity of the soft mode as a function of $P - P_c$ in a log-log scale for a constant temperature indicated according to Eq. (3) within the pressure interval (Table 2) in the paraelectric phase of SbSI.

Table 3. Values of the coefficients *a* and *b* according to Eq. (5) within the pressure intervals using the experimental data [1] for the soft mode frequency at constant temperature indicated. Values of the critical pressure (P_c), which were obtained from the w^2 vs. *P* plots [1] are also given here.

T (K)	241	231	202	150	119
P_c (kbar)	1.22	1.35	2.15	3.51	4.50
a $(cm^{-1})^2$/kbar	1124.63	1082.51	917.50	733.06	676.77
b $(cm^{-1})^2$	130.34	239.16	145.83	121.92	39.76
Pressure Interval (kbar)	$0.05 < P_c - P < 0.55$	$0.05 < P_c - P < 0.45$	$0.1 < P_c - P < 0.7$	$0 < P_c - P < 1$	$0 < P_c - P < 1.2$

phase of SbSI, as observed experimentally [1]. Discontinuity in *I(0)* disappears at $P_c = 1.4$ kbar and the tricritical point occurs at T≈234 K in this crystal [1].

As the pressure decreases in the ferroelectric phase, the Raman intensity of the soft mode increases smoothly, which was observed experimentally from the Raman and elastic light scattering [1].

Our analysis of the Raman intensity for this soft mode as a function of pressure gives the value of $\varphi' = 0.20$ for the critical exponent of the order parameter (Raman Intensity) at T = 234.2 K ($P_c = 1.4$ kbar) according to Eq. (2) in the ferroelectric (FE) phase (Table 1) of SbSI. The tricritical value for the order parameter is 0.25 according to the mean field model. This indicates that the tricritical behavior occurring within the pressure range of $1.322 < P$ (kbar) < 1.396 at T = 234.2 K (Fig. 4) in SbSI is adequately described according to our analysis given here by the mean field theory.

In fact, using the Landam phenomenological model, the temperature dependence of the spontaneous polarization P_s was described near the tricritical point with the tricritical exponent value of $\beta = 1/4$ for SbSI [1]. Also, the temperature dependence of the susceptibility χ was described with the critical exponent value of $\gamma = 1$ for the tricritical and continuous (second order) transitions in SbSI [1].

In our analysis, the exponent value ($\varphi = 0.32$), increases in the PE phase at T = 234.2 K (Table 2), indicating a continuous (second order) transition which takes place above tricritical point (Fig. 5), as compared to the mean field value of $\beta = 0.5$ for a second order transition. In regard to the pressure dependence of the intensity of the soft mode associated with the ferroelectric- paraelectric transition in SbSI at 272 K, our exponent value is $\varphi' = 0.18$, just below T_c (Table 1) in the pressure range of $\Delta P = 0.07$ kbar.

This indicates a first order transition since there is a discontinuous change in the intensity *I(0)*, as observed experimentally [1], whereas just above T_c in the pressure range of $\Delta P = 0.012$ kbar (Table 2) our exponent value ($\varphi = 0.56$) approaches the mean field value ($\beta = 0.5$) for a second order transition. However, above this pressure range ($0.477 < P$(kbar) < 0.501) the exponent value decreases to $\varphi = 0.15$ (Table 2) as in the ferroelectric phase (Table 1) indicating a first order line that appears in this pressure range of the paraelectric phase of SbSI. The existence of another tricritical point at $P = 0.477$ kbar (T = 272 K) between the first order and second order lines in SbSI can be questioned. More accurate experimental data from the spectroscopic measurements of the intensity of this soft mode at various pressures (T = 272 K) in the pressure range of $0.465 < P$(kbar) < 0.501 in the paraelectric phase ($P > P_c$), can make it clear if there exists a tricritical point (TCP) at $P = 0.477$ kbar.

In the second part of this study, we analyzed the pressure dependence of the Raman frequencies for the soft mode, which were measured [1] as a function of pressure at constant temperatures for the ferroelectric – paraelectric transition in SbSI. Linear plots of w^2 versus $P_c - P$ were obtained in the ferroelectric (FE) phases according to Eq. (5) as also obtained previously [1]. According to the soft–mode theory, the frequency decreases to zero as the transition point is approached. In the case of ferroelectric – paraelectric transition in SbSI, the Raman frequency of the soft mode exhibits the soft–mode behavior as a function of the pressure at constant temperatures. So that a linear variation of w^2 against $P_c - P$ and the occurrence of the tricritical behavior at T = 234 K (P_c = 1.4 kbar) are expected, as also observed experimentally [1] from the pressure dependence of the Raman frequency squared (w^2) of the soft mode in SbSI.

5. Conclusions

Pressure dependence of the Raman intensity and frequency of a soft mode associated with the ferroelectric – paraelectric transition in SbSI, was analyzed at constant temperatures of T = 272 and T = 234 K using the experimental data from the literature. Discontinuous change in the Raman intensity appearing at T = 272 K (first order transition) changes to a tricritical transition (continuity in the Raman intensity) at T = 234 K (P_c = 1.4 kbar) in the SbSI crystal, as observed experimentally. From our analysis of the Raman intensity according to a power–law formula, values of the critical exponent for the order parameter were deduced and they are compared with the predictions of the mean field theory. Our analysis indicates that the ferroelectric – paraelectric transition can be described by the mean field theory. Also, a linear variation of the frequency (squared) with the pressure was obtained at various constant temperature in SbSI, as obtained experimentally and the fitting parameters were determined.

We conclude the existence of the tricritical point (T = 234 K, P = 1.4 kbar) in SbSI can be investigated by means of the analysis given in this study.

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