Temperature Dependence of The Raman Frequency Shifts Related to The Specific Heat and Thermal Expansion Close To I-II Phase Transition in S-Triazine.

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ABSTRACT

A linear variation of the specific heat C_P with the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ is established for the Raman modes I-V at various temperatures (P=0) close to I-II phase transition in s-triazine (T_c=198 K).

As an extension of this work, the temperature dependence of the thermal expansion α_p is predicted from the frequency shifts and by the γ_p values deduced for the Raman modes studied close to the I-II phase transition in s-triazine.

Our predicted α_p can be examined by the thermodynamics measurements of the thermal expansion at various temperatures at zero pressure in both phases I and II of s-triazine.

Keywords: Raman modes. Frequency shifts. Phase transition. s-triazine.

1. INTRODUCTION

A structural phase change occurs in s-triazine at about 198 K /1/, as observed experimentally by x-ray diffraction and adiabatic calorimetry /2, 3/. This is the I-II phase transition as the temperature decreases. The crystal structure of the high-temperature phase (I) of s-triazine belongs to the rhombohedral space group $R\bar{3}c$ /4/. This transforms to a triply-twinned monoclinic phase (II) with decreasing temperature below T_c. It is a reversible temperature induced transformation to a lower symmetric phase accompanied by twinning /1/.

It has been reported that the low temperature structure (phase II) can be generated from the high-temperature hexagonal form (phase I) by shearing the crystal in the ac* plane and rotating the molecules about the b-axis /2/. Thus, the shear and rotation angles have been measured as a function of temperature in the temperature range 110 to 198 K in phase II /2/. As observed by the measurements of coherent inelastic neutron scattering /5, 6/ and Brillouin scattering /7/, Rae /8/ has studied the I-II transition by proposing that it is accompanied with a soft acoustic mode.

Several experimental studies have been carried out to investigate the mechanism of the I-II phase transition in s-triazine. The measurements associated with the I-II phase transition in s-triazine at low pressures on the specific heat /3/ and nuclear quadrupole resonance /9/, have been reported.

Various theoretical studies regarding I-II transition in s-triazine have also been reported in the literature /8, 10-14/. Very recently, we have analyzed the temperature dependence of the observed specific heat

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/3/ close to the I-II phase transition in s-triazine according to power-law formula /15/. We have calculated the specific heat using the quasi-harmonic and mean field approximation for s-triazine /16/. In order to understand the dynamical properties of the I-II transition in s-triazine, we have also studied the temperature dependence of the damping constant /17/.

The Raman spectra of s-triazine have revealed the mechanism of I-II phase transition under various temperatures and pressures. The Raman measurements of s-triazine have been conducted by several workers /18-22/. The Raman modes of I-V have been observed at various temperatures at atmospheric pressure in the phases I and II of s-triazine /21/. They have also been observed as a function of pressure at room temperature in the pressure range of 0 to 5 kbar (phase I) and from 5.1 to 40.5 kbar (phase II) in s-triazine /22/. Among those Raman modes, bands I and II have been assigned as the low frequency E_g mode of the high- temperature phase (phase I), and also bands IV and V as the high frequency E_g mode of phase I /21/. Thus, the low frequency E_g mode of the high-temperature phase (I) splits into the Raman bands I and II in the low-temperature phase (phase II). Also, the high frequency E_g mode of phase I splits into the Raman bands IV and V in phase II, as pointed out previously /21/. The Raman band III which is unobservable above 170 K, corresponds to the molecular motions R_z and T_z, and it is Raman inactive in the high-temperature phase I /21/.

In this study, using the observed frequencies of the Raman modes I-V /21/ and the observed specific heat C_p data /3/, at various temperatures at zero pressure, we establish the spectroscopic modification of the Pippard relation close to the I-II phase transition in s-triazine. This gives a linear variation of C_p with the frequency shifts $\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P$ for the Raman modes studied here in s-triazine. From linear plots of C_p against $\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P$, values of the isobaric mode Grüneisen parameter γ_p are extracted for the Raman modes in both phases I and II, and the thermal expansion α_p is calculated as a function of temperature close to the I-II phase transition in this molecular crystal.

Below, we give in section 2 our calculations for the $\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P$, γ_P and α_p in phases I and II of s-triazine. In section 3 our discussion about the results is given. Finally, conclusions are given in section 4.

2. CALCULATIONS AND RESULTS

The specific heat C_P can be related to the thermal expansion α_p close to the I-II transition in s-triazine according to the Pippard relation

$$C_P = T\left(\frac{dP}{dT_c}\right)\alpha_p V + T\left(\frac{dS}{dT}\right)_t \tag{1}$$

In Eq.(1) the slope dP/dT_c and the variation of entropy with the temperature, $(dS/dT)_t$ are taken at the transition temperature T_c (198 K) in s-triazine. V is the crystal volume. By the mode Grüneisen parameter γ, the crystal volume can be related to the vibrational frequency ω according to

$$\gamma = -\frac{V}{\omega}\frac{d\omega}{dV} \tag{2}$$

or by defining isobaric mode Grüneisen parameter γ_p as

$$\gamma_P = -\frac{1}{\alpha_P}\cdot\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P \tag{3}$$

where the thermal expansion $\alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. The Pippard relation given by Eq.(1) can be written as

$$C_P/R = -\frac{TV}{\gamma_P}\left(\frac{dP}{dT}\right)_c\cdot\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P + T\left(\frac{dS}{dT}\right)_t \tag{4}$$

Here R is the gas constant. This relates the specific heat C_P to the variation of the vibrational frequency with the temperature (frequency shift), $\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P$. Thus, the specific heat C_P measured thermodynamically can be plotted as a function of the frequency shifts, $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$, measured spectroscopically at various temperatures for a constant pressure (P=0) close to the I-II phase transition in s-triazine according to Eq.(4). This linear plot gives the value of the mode Grüneisen parameter γ_p for the relevant phonon by knowing the values of the slope (dP/dT_c) and the crystal volume at $T=T_c$.

In this study, we established the Pippard relation modified spectroscopically (Eq.(4)) using the observed specific heat C_p /3/ and the observed Raman frequencies of the modes I, II, III, IV and V /21/ at various temperatures (zero pressure) in phases I and II (T_C = 198 K) in s-triazine. A linear relationship was established between C_P and the Raman frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ for the five Raman modes (I-V) close to the I-II phase transition in the phases I ($T>T_c$) and II ($T<T_c$) in s-triazine according to Eq.(4). From this linear relationship, the values of the mode Grüneisen parameter γ_p were obtained for the Raman modes studied here. For this procedure, we first fitted with Eq.(5) to the temperature dependence of the measured Raman frequencies /3/ for the modes I and IV in the phase I ($T>T_c$), and then to the Raman frequencies for the modes I, II, III, IV and V in phase II ($T<T_c$).

$$\omega = a + bT \tag{5}$$

Table 1 gives the fitted parameters a and b for all the modes studied here. We then determined $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ as a function of temperature for the Raman modes in phase I (modes I and IV) and in phase II (modes I-V). Thus, the observed specific heat C/R /3/, was plotted against the Raman frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ for those modes according to Eq.(4) for the phases I and II in s-triazine.

Table 1

Values of the parameters a and b according to Eq.(5) for the observed frequencies /21/ of the Raman modes indicated at various temperatures in the phases I and II of s-triazine

T_c=198.07 K	$T > T_c$ (Phase I)		$T < T_c$ (Phase II)	
Raman modes	$a \times 10^{-2}$ (m^{-1})	$-b \times 10^{-2}$ (m^{-1} /K)	$a \times 10^{-2}$ (m^{-1})	$-b \times 10^{-2}$ (m^{-1} /K)
I	82.80	0.052	81.43	0.027
II	-	-	97.89	0.125
III	-	-	92.05	0.049
IV	114.58	0.075	111.96	0.061
V	-	-	126.32	0.133

Figures 1 and **2** give C/R against $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ of the Raman mode I for the phases I ($T>T_c$) and II ($T<T_c$) of s-triazine, respectively according to Eq.(4). Since mode II appears in the Raman spectra of s-triazine in phase II only /21/, variation of C/R with the frequency shifts of this mode is plotted in **Figure 3**. Similarly, mode III appears only in phase II ($T<T_c$) as the Raman mode II /21/. We plot C/R against the $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ of the Raman mode III for phase II ($T<T_c$) in **Figure 4.** For the Raman mode IV, variation of C/R with the $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ in phases I and II, is plotted in **Figure 5** and **Figure 6**, respectively. Also, the Raman mode V exists in phase II ($T<T_c$) only similar to the Raman modes II and III /21/. **Figure 7** gives our plot of C/R against $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ for the Raman mode V below T_c (phase II) in s-triazine.

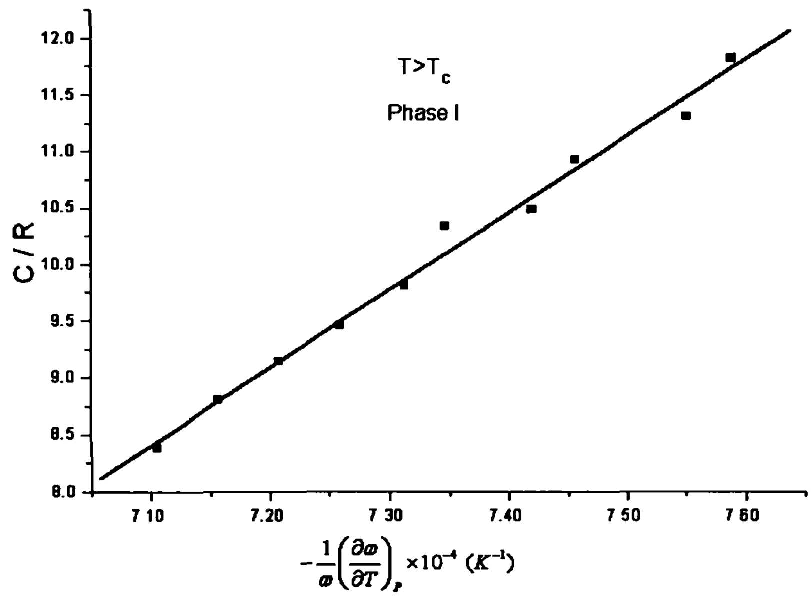

Fig. 1: Observed specific heat *C/R* /3/ (*R* is the gas constant) as a function of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ obtained from the observed Raman frequencies /21/ at various temperatures (P=0) for the Raman mode I according to Eq.(4) above the transition temperature (T_c=198.07 K) in the phase I of s-triazine.

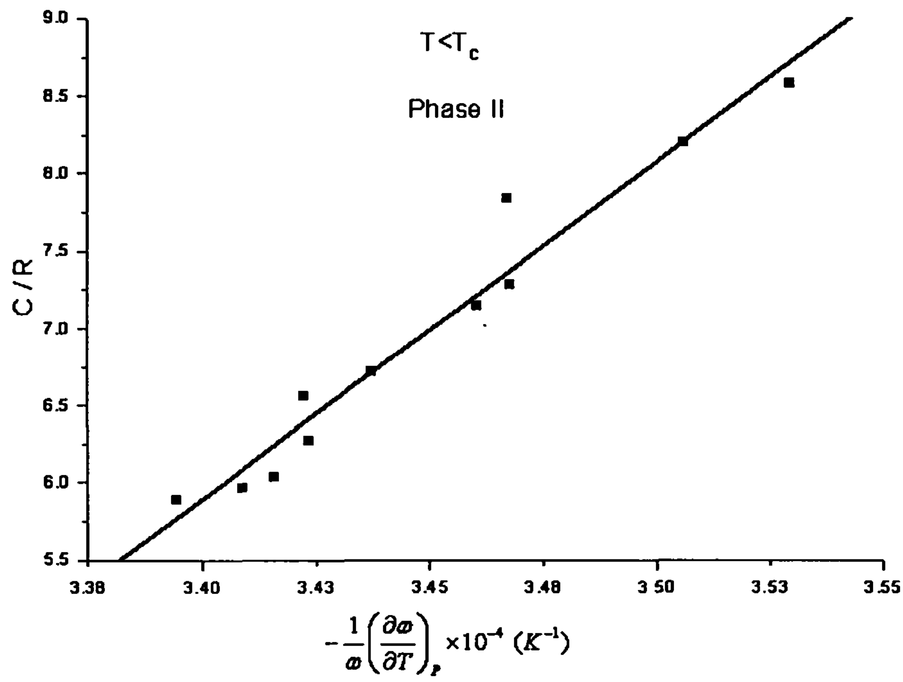

Fig. 2: Observed specific heat *C/R* /3/ (*R* is the gas constant) as a function of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ obtained from the observed Raman frequencies /21/ at various temperature (P=0) for the Raman mode I according to Eq.(4) below the transition temperature (T_c=198.07 K) in the phase II of s-triazine.

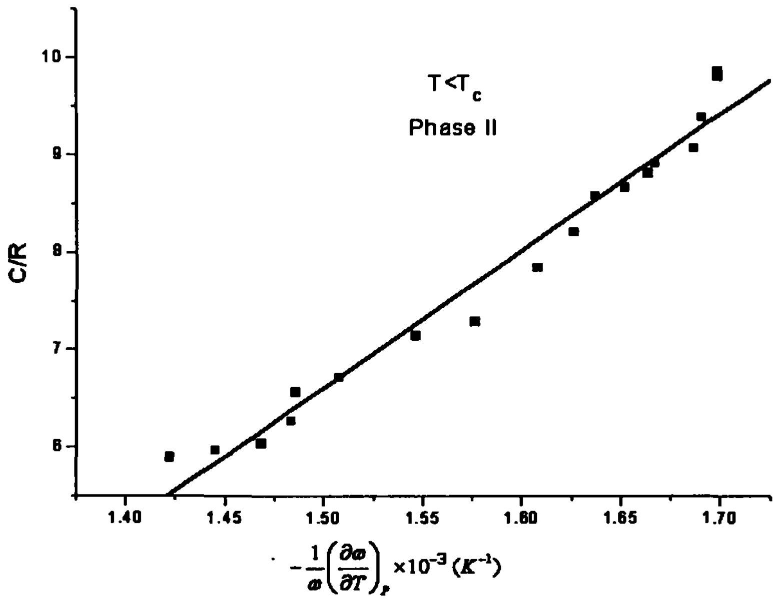

Fig. 3: Observed specific heat *C/R* /3/ (*R* is the gas constant) as a function of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ obtained from the observed Raman frequencies /21/ at various temperatures (P=0) for the Raman mode II according to Eq.(4) below the transition temperature (T_c=198.07 K) in the phase II of s-triazine.

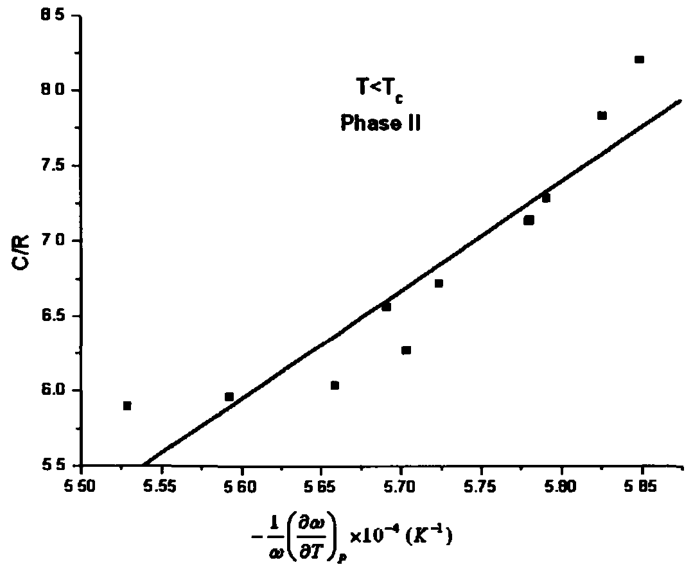

Fig. 4: Observed specific heat *C/R* /3/ (*R* is the gas constant) as a function of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ obtained from the observed Raman frequencies /21/ at various temperatures (P=0) for the Raman mode III according to Eq.(4) below the transition temperature (T_C=198.07 K) in the phase II of s-triazine.

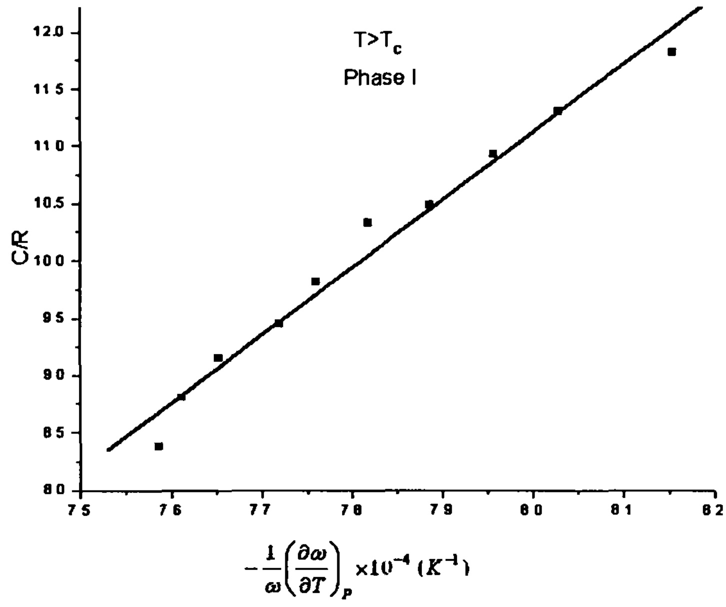

Fig. 5: Observed specific heat *C/R* /3/ (*R* is the gas constant) as a function of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P$ obtained from the observed Raman frequencies /21/ at various temperatures (*P*=0) for the Raman mode IV according to Eq.(4) above the transition temperature (T_c=198.07 K) in the phase I of s-triazine.

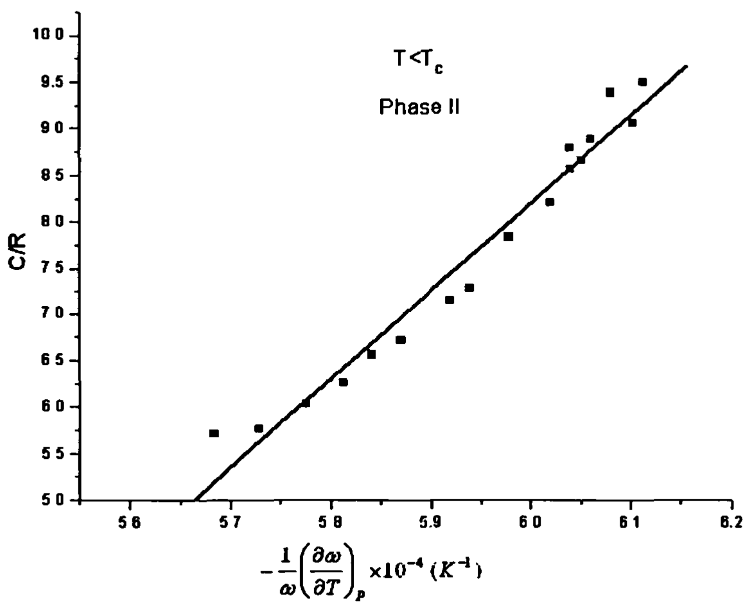

Fig. 6: Observed specific heat *C/R* /3/ (*R* is the gas constant) as a function of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P$ obtained from the observed Raman frequencies /21/ at various temperatures (*P*=0) for the Raman mode IV according to Eq.(4) below the transition temperature (T_c=198.07 K) in the phase II of s-triazine.

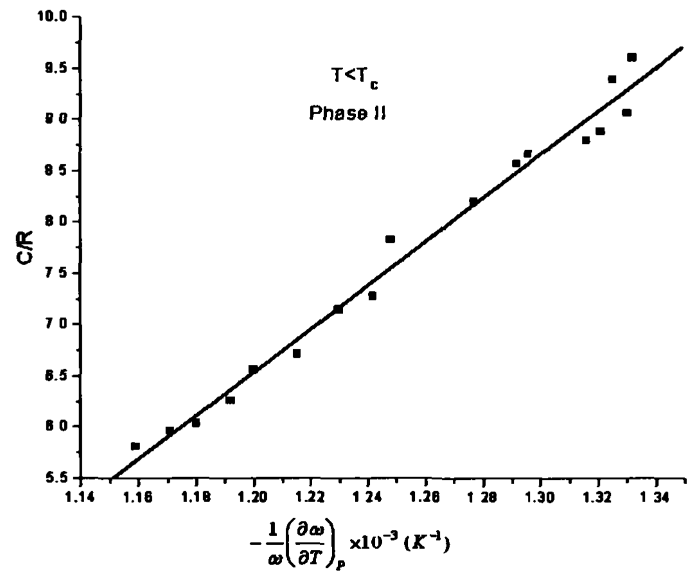

Fig. 7: Observed specific heat *C/R* /3/ (*R* is the gas constant) as a function of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ obtained from the observed Raman frequencies /21/ at various temperatures (P=0) for the Raman mode V according to Eq.(4) below the transition temperature (T_c=198.07 K) in the phase II of s-triazine.

We extracted the values of the mode Grüneisen parameter γ_p for the Raman modes I-V studied here from our plots of the specific heat *C/R* against the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$, as given in Figures (1-7) according to Eq.(4). The γ_p values of those modes were determined for both phases I ($T>T_c$) and II ($T<T_c$) in s-triazine. Since the modes II and V do not appear in the Raman spectra /21/ in phase I ($T>T_c$), we considered here that they were originated from the modes I and IV, respectively, in the phase I. So that, we took the same γ_p value for the Raman mode II as the mode I in phase I ($T>T_c$). Also, we assumed the same γ_p values for the Raman mode V as the mode IV in phase I ($T>T_c$). Due to the fact that the Raman mode III appears only in phase II ($T<T_c$), as stated above, we were unable to extract its γ_p value in phase I ($T>T_c$). **Table 2** gives our values of the mode Grüneisen parameter γ_p for the Raman modes I-V in the phases I and II with the values of the intercept $(dS/dT)_t$ at the transition temperature (T_c=198.07 K) for the I-II transition in s-triazine. When we determined the γ_p values from our plots of *C/R* against $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ from Eq.(4), we used the slope value of the transition temperature according to the empirical relation

$$T_c=198 + 18.7\,P \tag{6}$$

which was obtained experimentally in the *P-T* phase diagram /23, 24/, as also given in the previous work /22/. In Eq.(6), T_c is in the units of Kelvin (K) and the pressure in kbars. So, the $(dP/dT)_c$=5.348 MPa/K(=53.48 bar/K) was obtained from Eq.(6), which was used in Eq.(4). The volume V value was obtained from the density value of ρ=1376 kg/m^3 /4/ and the mass value of M=81x10^{-3} kg/mol of s-triazine ($C_3H_3N_3$), which gave V=58.866x10^{-6} m^3/mol. Using those values of T_c =198.07 K, $(dP/dT)_c$ and V, the γ_p values for the Raman modes (I-V) were extracted from Eq.(4), as given in Table 2.

Table 2

Values of the isobaric mode Grüneisen parameter γ_p for the Raman modes indicated and the values for the variation of the entropy with the temperature, $(dS/dT)_t$ (normalized with the gas constant R because of the observed specific heat C/R /3/) at the transition temperature T_c in the phases I and II of s-triazine according to Eq.(4).

T_c=198.07 K	$T > T_c$ (Phase I)		$T < T_c$ (Phase II)	
Raman modes	γ_p	$-(dS/dT)_t$ (K^{-1})	γ_p	$-(dS/dT)_t$ (K^{-1})
I	0.91	0.20	0.29	0.34
II	0.91	0.20	4.44	0.07
III	-	-	0.86	0.18
IV	1.06	0.18	0.66	0.25
V	1.06	0.18	2.95	0.10

As an extension of this study, we also calculated here the temperature dependence of the thermal expansion α_p by knowing the values of the mode Grüneisen parameter γ_p of the Raman modes considered (Table 2), according to Eq.(3). By using the temperature dependence of the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$, the α_p values were calculated as a function of temperature.

Figures 8 and **9** give the temperature dependence of the thermal expansion α_p calculated from the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ of the Raman modes I and II, respectively. As shown in Figure 9, we had the same α_p values calculated using the $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ values of the Raman mode II as the Raman mode I (Figure 8) above T_c (phase I) with the same γ_p value (Table 1) since the modes I and II in phase II merge to give a single Raman mode in phase I ($T > T_c$), as observed experimentally /21/.

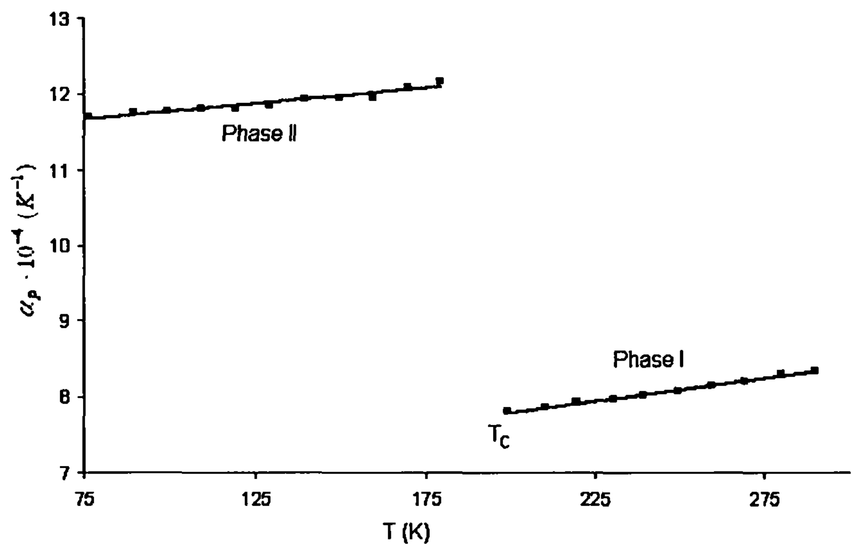

Fig. 8: Temperature dependence of the thermal expansion α_p calculated from Eq.(3) using the observed Raman frequencies /21/ of the mode I close to the I-II phase transition in s-triazine (T_c=198 K).

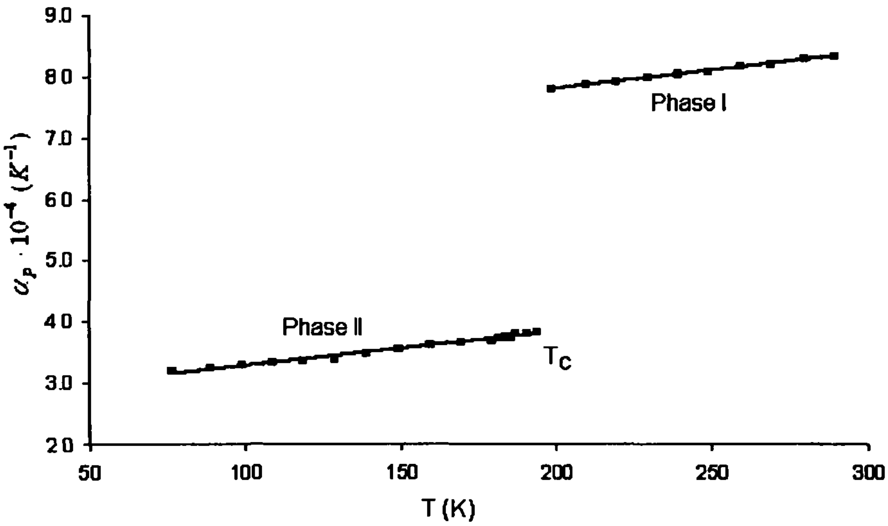

Fig. 9: Temperature dependence of the thermal expansion α_p calculated from Eq.(3) using the observed Raman frequencies /21/ of the mode II close to the I-II phase transition in s-triazine (T_c=198 K).

Figure 10 gives the thermal expansion α_p as a function of temperature below T_c (phase II) in s-triazine, which was calculated using the Raman frequencies of the mode III according to Eq.(3). Since there was no observed frequency data for this mode above T_c /21/, we were not able to calculate the temperature dependence of α_p in phase I. We also plot the thermal expansion α_p calculated using the $\frac{1}{\omega}\left(\frac{\partial \omega}{\partial T}\right)_P$ values of the Raman modes IV and V as a function of temperature in **Figure 11** and **Figure** 12, respectively. For the same reason as the Raman modes I and II, we considered that the modes IV and V in phase II ($T<T_c$) merge to give a single mode in phase I ($T>T_c$), as observed experimentally /21/. So that we obtained the same values of the thermal expansion α_p above T_c for both modes IV (Figure 11) and V (Figure 12).

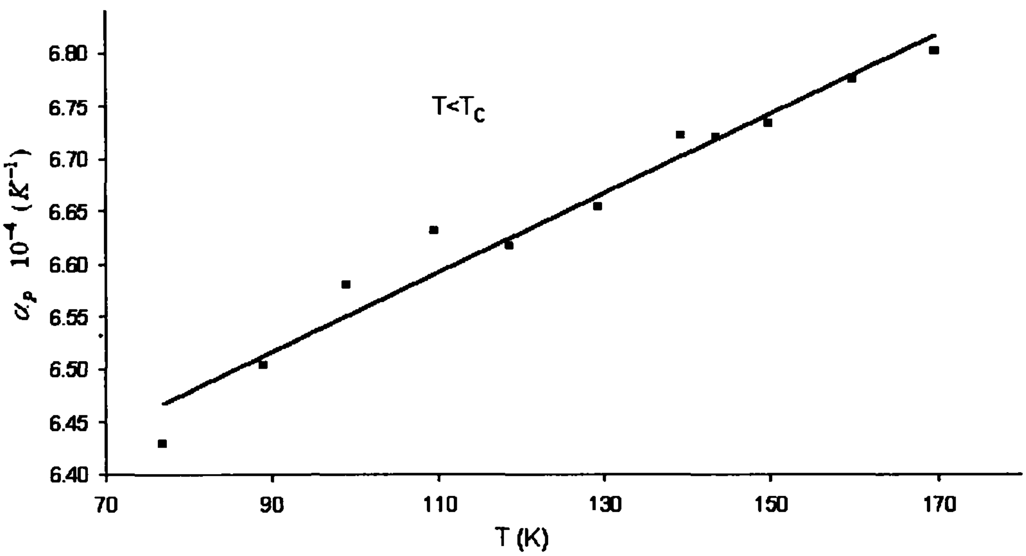

Fig. 10: Temperature dependence of the thermal expansion α_p calculated from Eq.(3) using the observed Raman frequencies /21/ of the mode III in phase II of s-triazine (T_c=198K).

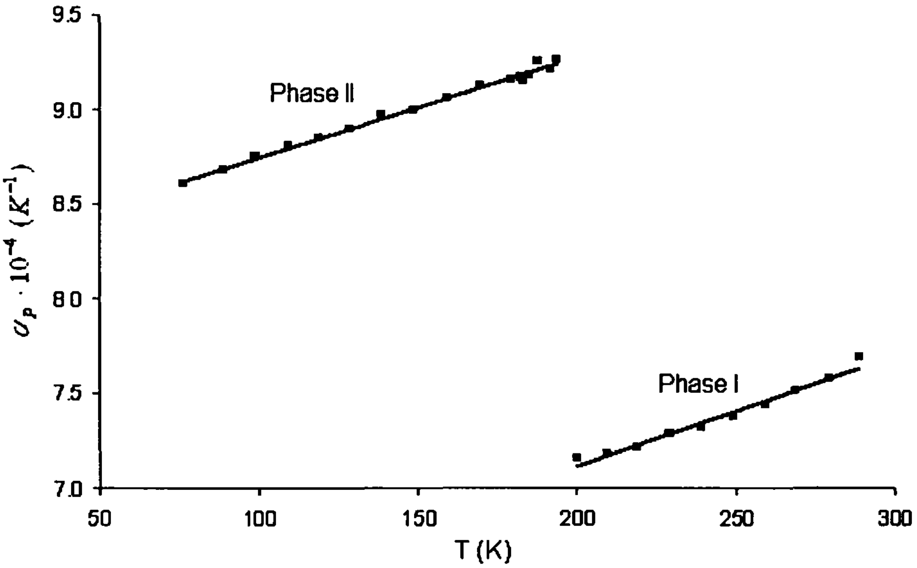

Fig. 11: Temperature dependence of the thermal expansion α_p calculated from Eq.(3) using the observed Raman frequencies /21/ of the mode IV close to the I-II phase transition in s-triazine (T_c=198 K).

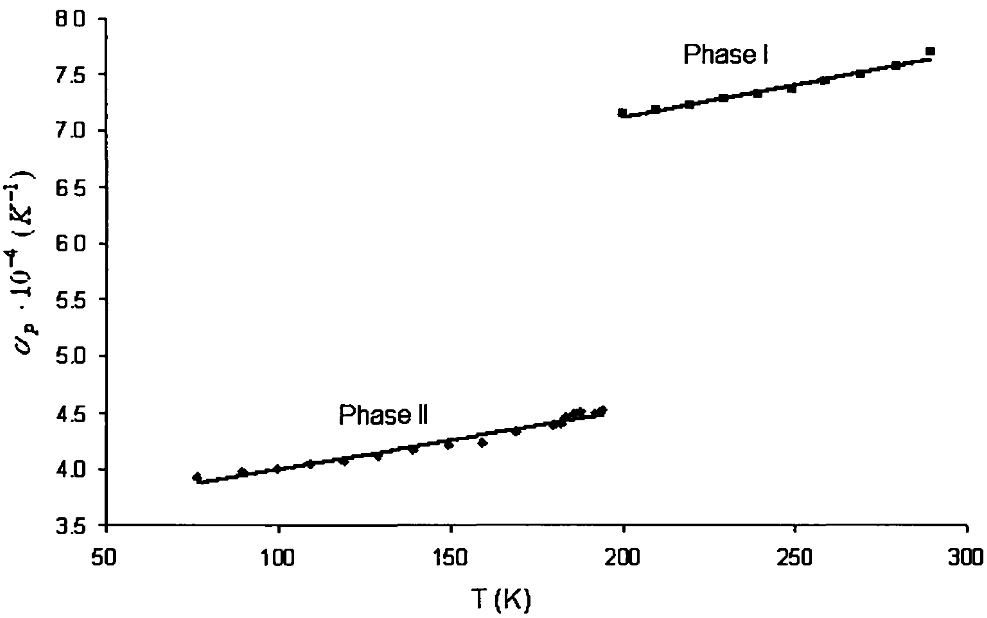

Fig. 12: Temperature dependence of the thermal expansion α_p calculated from Eq.(3) using the observed Raman frequencies /21/ of the mode V close to the I-II phase transition in s-triazine (T_c=198 K).

3. DISCUSSION

A linear variation of the specific heat C/R with the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ was established at various temperatures in phases I ($T>T_c$) and II ($T<T_c$) of s-triazine, as shown in Figures (1-7). This was obtained in both phases I and II using the frequencies of the Raman modes I and IV. Linear plots of C/R against $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ were obtained for the Raman modes II, III and V in phase II ($T<T_c$) only since there was no Raman data /21/

in phase I ($T>T_c$) for those modes considered. Thus, Figures (1-7) show that there is a linear relationship between the specific heat C/R and the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ close to the I-II transition in s-triazine according to the spectroscopic modification of the Pippard relation (Eq.4)

From the linear plots of C/R against $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ (Figures 1-7), the values of the mode Grüneisen parameter γ_P were deduced for the Raman modes I to V in phase II ($T<T_c$), as tabulated in Table 2. In phase I ($T>T_c$) the γ_P values were determined for the Raman modes I to V except the Raman mode III since there were no observed frequencies /21/ in this phase of s-triazine. In phase I ($T>T_c$) the value of $\gamma_P \approx 1$ was obtained for the Raman modes of I, II, IV and V, whereas the γ_P values varied from 0.3 to nearly 4 for all the modes I to IV in phase II ($T<T_c$) in s-triazine (Table 2).

We also deduced the values of the $(dS/dT)_t$ from Eq.(4) for the phases I ($T>T_c$) and II ($T<T_c$) of s-triazine, as given in Table 2. The $(dS/dT)_t$ values obtained from the Raman frequencies of the modes I, II, IV and V, were the same as nearly 0.2 in phase I ($T>T_c$) (Table 2). For the phase II ($T<T_c$), the values of $(dS/dT)_t$ varied from 0.1 to 0.3 K^{-1} which were obtained from the Raman frequencies of all the modes (I to V) in s-triazine (Table 2)

Since we determined the values of the isobaric mode Grüneisen parameter γ_P for the Raman modes studied here in the phases I ($T>T_c$) and II ($T<T_c$), we were able to calculate the thermal expansion α_P as a function of temperature according to Eq.(3), as given in Figures (8-12). The α_P was calculated as a function of temperature, using the Raman frequencies of the mode III in phase II ($T<T_c$) only, since we were able to determine its γ_P value in this phase (Table 2), as given in Figure 10. The temperature dependence of the thermal expansion α_P exhibits similar critical behaviour due to the Raman modes I (Figure 8) and IV (Figure 11), which jumps considerably to the lower values with increasing temperature in s-triazine. On the other hand, the critical behavior of the thermal expansion α_P is similar that was calculated from the Raman frequencies of the modes II (Figure 9) and V (Figure 12). The α_P increases with increasing temperature by exhibiting a jump at T_c, as shown in Figures 9 and 12. We note that the α_P has the same values in phase I ($T>T_c$), which were obtained from the Raman frequencies of the modes I and II (Figures 8 and 9). Also, the α_P values are the same in phase I ($T>T_c$), which was obtained using the Raman frequencies of the modes IV and V, as given in Figures 11 and 12, respectively. By extending the α_P to the transition temperature T_c=198.07 K from both phases I ($T>T_c$) and II ($T<T_c$), we calculated their values, as tabulated in Table 3.

Table 3

Values of the thermal expansion α_P extended to the transition temperature (T_c=198.07 K) from both phases I ($T>T_c$) and II ($T<T_c$), which were calculated using the Raman frequencies of the modes indicated according to Eq.(3). Difference in the α_P values at T_c, (Eq. 7) $\Delta\alpha_P = \alpha_P(T>T_c) - \alpha_P(T<T_c)$, is also given here.

T_c=198.07 K	$T>T_c$ (Phase I)	$T<T_c$ (Phase II)	$T=T_c$ (K)
Raman Modes	$\alpha_P \times 10^{-4}$ (K^{-1})	$\alpha_P \times 10^{-4}$ (K^{-1})	$\Delta\alpha_P \times 10^{-4}$ (K^{-1})
I	7.80	12.20	-4.40
II	7.80	3.84	3.96
III	-	6.94	-
IV	7.11	9.27	-2.16
V	7.11	4.52	2.59

They were calculated using the Raman frequencies of the modes I, II, III (phase II only), IV and V according to Eq.(3) by using the values of the mode Grüneisen parameter γ_p (Table 2). We also give the values of the difference (jump) in α_p which we defined as

$$\Delta\alpha_P = \alpha_P(T > T_c) - \alpha_P(T < T_c) \qquad (7)$$

due to the Raman modes studied in s-triazine. For the Raman modes I and II, the difference in α_p is about the same with the decreasing (-) and increasing (+) values, as the temperature decreases from phase I ($T>T_c$) to phase II ($T<T_c$). Also, the $\Delta\alpha_p$ value is nearly the same for the Raman modes IV and V with the decreasing (-) and increasing (+) values, as before.

The critical behaviour of the thermal expansion α_p which we predicted in this study using the Raman frequencies of the modes considered, can be examined by the measurements of the α_p at various temperatures (P=0) close to the I-II phase transition in s-triazine. From the thermodynamics measurements, the change in the thermal expansion at T_c, $\Delta\alpha_p$, can also be determined and it can then be compared with our calculated values given in Table 3.

4. CONCLUSIONS

The spectroscopic modification of the Pippard relation was constructed by a linear variation of the specific heat C/R with the frequency shifts $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ close to the I-II phase transition in s-triazine. The observed specific heat and the observed frequencies of the Raman modes I, II, III, IV and V were used for this linear variation of C/R with the $\frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_P$ in phases I and II of s-triazine. From linear plots, the values of the isobaric mode Grüneisen parameter γ_p were extracted for the Raman modes studied here. By means of the γ_p values, the thermal expansion α_p was calculated as a function of temperature at zero pressure close to the I-II phase transition in s-triazine.

Measurements of the length-change or the lattice parameter which can be conducted at various temperatures (P=0), can be compared with our predictions of the thermal expansion α_p near the I-II phase transition in s-triazine.

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