# Calculation of the Specific Heat Close to Phase Transition in S-triazine

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## ABSTRACT

The specific heat $C_V$ as a function of temperature has been calculated using the quasi-harmonic and mean field approximation for s-triazine close to the transition temperature ($T_C$=198 K). Using the parameters for the shear strain angle (order parameter) fitted to the observed Raman frequencies of the four bands, the specific heat $C_V$ is calculated from the free energy of s-triazine.

The calculated $C_V$ values show no anomaly in comparison with the experimentally observed $C_P$ which exhibits a sharp peak near $T_C$ in s-triazine.

**Keywords:** specific heat, mean field model, s-triazine.

## 1. INTRODUCTION

The ferro-elastic phase transition from the high temperature (phase I) to the low temperature (phase II) in s-triazine at $T_C$ = 198 K as the temperature decreases, has been the subject of a number of studies in the literature. The crystal structure changes from the hexagonal (phase I) to the monoclinic (phase II) as detected in the X-ray diffraction pattern /1/. The low temperature structure can be generated from the high-temperature hexagonal form by shearing the crystal in the $a^*c$ plane and rotating the molecules about the b axis. Thus, in the low-temperature monoclinic phase, the angle of rotating $\varphi$ appears which is proportional to the shear strain angle $\theta$, and they both increase discontinuously just below $T_C$ accompanied with a continuous increase at low temperatures /2/, as obtained experimentally in Fig.1. This steady decrease of the shear strain angle $\theta$ with increasing T towards $T_C$, has been considered as the behaviour of the order parameter in a quasi-continuous or nearly second order phase transition in s-triazine /2/. This was also supported by a small latent heat discontinuity at around 198 K from the specific heat $C_P$ measurements for s-triazine /3/.

The mechanism of a proper ferro-elastic phase transition in s-triazine has been explained by an acoustic mode that softens at the Brillouin zone centre by Rae /4/, as observed experimentally /5/. Raich and Bernstein /6/ have explained the mechanism of phase transition in s-triazine by means of a coupling between rotational and translational modes of motion. From the Raman measurements, it has been detected that the higher-frequency $E_g$ mode is translational and that the lower-frequency $E_g$ mode is rotational /7/. It has also been detected that the low-frequency $E_g$ mode of the high temperature phase (phase I) splits into the Raman bands I and II, whereas the high-frequency $E_g$ mode splits into the Raman bands IV and V, as observed experimentally /7/. The frequencies of the Raman-active bands I, II, IV and V have been related to the shear strain angle $\theta$ (order parameter)in earlier studies /7, 8/.

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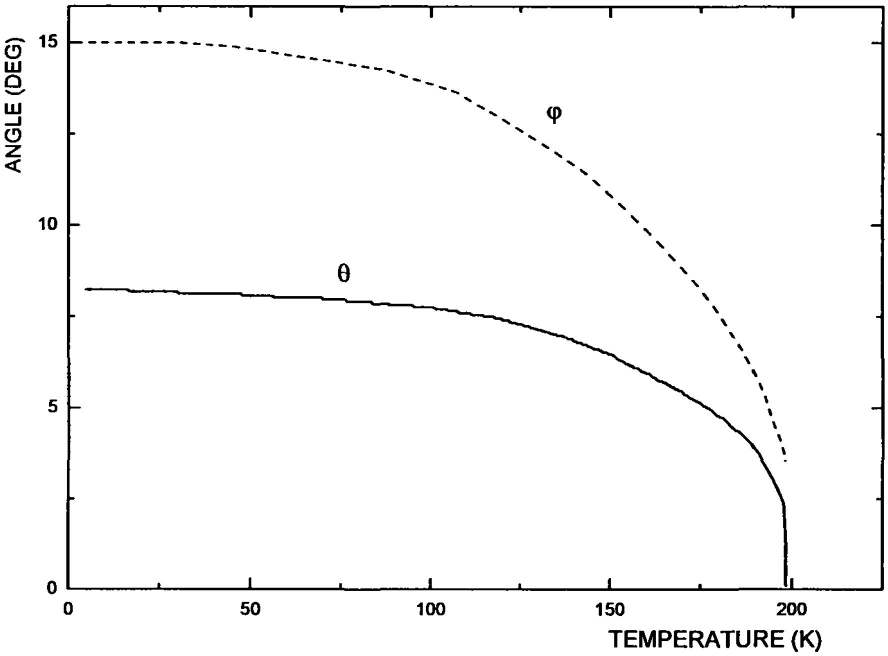

**Fig. 1:** The temperature dependence of the shear strain angle $\theta$ and molecular rotation angle $\varphi$ as order parameters for s-triazine, as determined by Smith and Rae /2/ and by Prasad et al. /13/.

Dynamical behaviour of the coupled system of molecular orientations and acustic phonons has been investigated to describe the ferro-elastic phase transitions /9/. Also, the temperature dependence of the halfwidth of the Raman band II has been measured experimentally and it has been concluded that there is no anomalous behaviour of the halfwidth in the vicinity of the transition temperature ($T_C$ = 198 K) /7/. Using the observed bandwidths for the Raman band II /7/, we have calculated the damping constant in terms of the order parameter as a function of temperature near the phase transition ($T_C$ = 198 K) in s-triazine by the soft mode-hard mode coupling model /10/ in our recent study /11/. Very recently, we have established the spectroscopic modifications of Pippard relations using the frequencies of the Raman modes in s-triazine /12/. The free energy can be expanded in terms of the shear angle $\theta$, or in terms of the normal mode coordinates of the Raman active phonons within the mean-field approximation. By means of this expansion, the free energy has been calculated as a function of temperature below $T_C$ in s-triazine /7, 8/. Thus the ferro-elastic phase transition in s-triazine has been described by the mean field theory using the Einstein model for the lattice vibrations in s-triazine /7, 8/. From the free energy functional which has mainly two parts; the crystal potential energy expanded in terms of the shear strain angle $\theta$ (order parameter) and a sum over the temperature dependence of the lattice frequencies (Einstein model), the specific heat $C_V$ can be calculated. In this study, the specific heat $C_V$ is calculated within the mean field approximation using the temperature dependence of the shear strain angle $\theta$ /8/ and of the observed Raman frequencies for the bands I, II, IV and V in the free energy functional /7/ to describe the ferroelastic phase transition ($T_C$ = 198 K) in s-triazine.

## 2. CALCULATION AND RESULTS

The thermodynamics quantities can be calculated near the phase transition in s-triazine ($T_C$=198 K) from the free energy according to the model described by Rae /8/ using quasi-harmonic and mean field approximations,

$$F = V(\theta) + T \cdot \sum_{i} \ln\left[2\sinh(\hbar\omega_i / 2k_B T)\right] \qquad (1)$$

as given previously /7/. In Eq. (1), $V(\theta)$ is the crystal potential energy which depends on the order parameter $\theta$ (shear strain angle). Below $T_C$, the temperature dependence of the order parameter (shear strain angle and molecular rotation angle) has been determined in earlier studies /2, 13/, as given Fig. 1. Shear strain angle $\theta$, in particular has been related to the frequencies of the Raman-active modes $\omega_I$ , $\omega_{II}$ , $\omega_{IV}$ and $\omega_V$ according to the relations /7/

$$\begin{aligned}\omega_I^2 &= \omega_0^2 + \alpha\cdot\theta + \beta_1\cdot\theta^2\\ \omega_{II}^2 &= \omega_0^2 - \alpha\cdot\theta + \beta_2\cdot\theta^2\\ \omega_{IV}^2 &= \omega_0'^2 + \alpha'\cdot\theta + \beta_1'\cdot\theta^2\\ \omega_V^2 &= \omega_0'^2 - \alpha'\cdot\theta + \beta_2'\cdot\theta^2\end{aligned} \tag{2}$$

In Eq. (2) $\omega_0$ and $\omega_0'$ are the Raman frequencies in the high-temperature phase ($T>T_C$) where the order parameter ($\theta$) is zero. The other coefficients, $\alpha$ , $\alpha'$, $\beta_1$, $\beta_1'$, $\beta_2$ and $\beta_2'$ are all constants. Ewen and Dove /7/ have fitted Eq. (2) to their observed frequencies of the Raman modes I, II, IV and V, and they have obtained the numerical coefficients of Eq. (2), as given in Table 1.

**Table 1**

Numerical coefficients of Eq. (2) obtained from the experimental Raman frequencies by Rae /8/ and by Ewen and Dove /7/ in s-triazine.

| | Ewen & Dove /7/ | Rae /8/ | |
|---|---|---|---|
| $\omega_0^2$ | 5314 | 5002 | $\times 10^{-4}\, m^{-2}$ |
| $\omega_0'^2$ | 9956 | 9231 | $\times 10^{-4}\, m^{-2}$ |
| $\alpha$ | 3700 | 4664 | $\times 10^{-4}\, m^{-2}\, rad^{-1}$ |
| $\alpha'$ | 2000 | 5679 | $\times 10^{-4}\, m^{-2}\, rad^{-1}$ |
| $\beta_1$ | 20800 | 3866 | $\times 10^{-4}\, m^{-2}\, rad^{-2}$ |
| $\beta_2$ | 101000 | 132200 | $\times 10^{-4}\, m^{-2}\, rad^{-2}$ |
| $\beta_1'$ | 17000 | 9666 | $\times 10^{-4}\, m^{-2}\, rad^{-2}$ |
| $\beta_2'$ | 134000 | 154700 | $\times 10^{-4}\, m^{-2}\, rad^{-2}$ |
| Cross-over temperatures | 178 | 189 | K |
| | >198 | 187 | K |

In this table the numerical coefficients of Rae /8/ have also been given for comparison, as indicated previously /7/. By taking the temperature dependence of the order parameter (shear strain angle), as determined experimentally (Fig. 1) with the numerical coefficients (Table 1), Rae /8/ and Ewen and Dove /7/ have calculated the free energy F at various temperatures below the transition temperature in s-triazine according to Eq. (1), as plotted in Fig. 2. In this figure the free energy represents the difference between the low-phase ($T<T_C$) and high-phase ($T>T_C$) energies. In the high-temperature phase, the order parameter $\theta$ was taken as zero in Eq. (1). This calculation of the free energy was done by obtaining the derivative of the crystal potential energy V with respect to the order parameter $\theta$, $\partial V/\partial\theta$, and by taking the potential energy zero in the high temperature ($T>T_C$) where the order parameter $\theta$ is zero. The transition temperature was taken as 198.35 K /8/ and 197.1 K /7/ to calculate the free energy F as a function of temperature (Fig. 2).

In this calculation below $T_C$, $\partial V/\partial\theta$ was obtained as a cubic polynomial, so that from the fitting the form of the potential $V(\theta)$ was evaluated /7/ as

$$V(\theta) = -30911\cdot\theta^2 - 49043\cdot\theta^3 + 666291\cdot\theta^4 \ J\ mol^{-1} \tag{3}$$

In this study, we calculated the temperature dependence of the specific heat $C_V$ for s-triazine according to the second derivative of the free energy with respect to the temperature at a constant order parameter $\theta$, $C_V = -T(\partial^2 F/\partial T^2)_\theta$. This was done by using Eq. (1) where the Einstein model has been assumed for the four Raman modes (I, II, IV and V) and minimizing the free energy with respect to the parameter $\theta$, which gives

$$\frac{\partial V}{\partial\theta} + \frac{1}{2}\sum_i \coth(\hbar\omega_i/2k_BT)\frac{\partial\omega_i}{\partial\theta} = 0 \tag{4}$$

as also given previously /7/. By means of the derivatives $\partial\omega_i/\partial\theta$ from Eq. (2) for the four Raman modes ($i$ = I, II, IV and V) and using the numerical coefficients (Table 1) with the $\theta$ dependence of the potential energy V (Eq. 3), the specific heat $C_V$ was calculated as a function of temperature, as plotted in Fig. 3. We calculated the specific heat $C_V$ as a function of temperature in the temperature interval from about 100 K up to 290 K (Fig. 3) which includes the temperature interval below $T_C$ for the free energy (Fig. 2). Cross-over temperatures are indicated in Table 1. In Fig. 3 we represent the $C_V$ values calculated using the observed Raman frequencies of the bands I, II, IV and V /7/ in Eq. (1), which we denoted by the symbol (●). We also represent the $C_V$ values calculated from the Raman frequencies evaluated by Eq. (2) using the $\theta$ values (Fig. 1) according to Eq. (1), which we denoted by the symbol (▲).

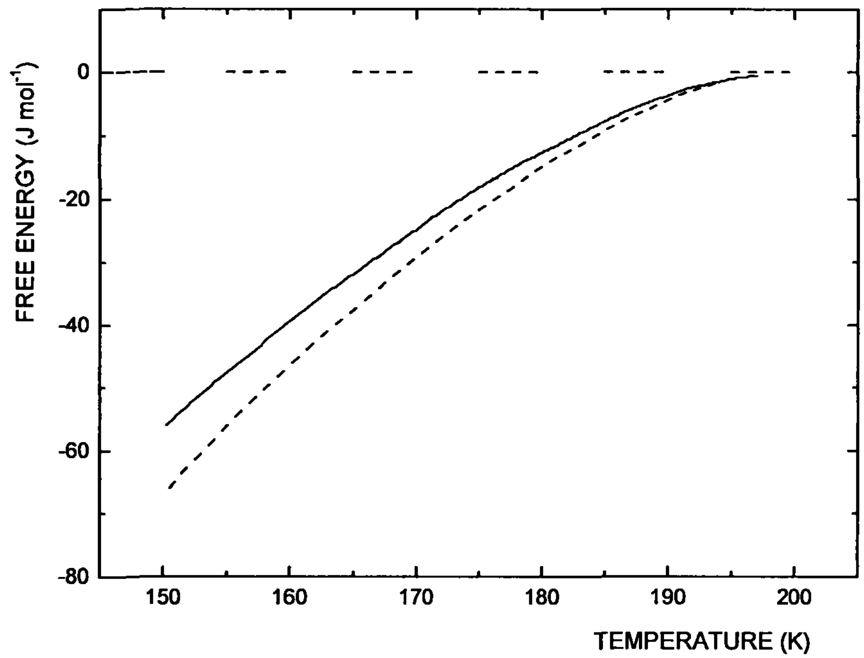

**Fig. 2:** Calculated free energy as a function of temperature using the parameters (Table 1) by Ewen and Dove /7/ (continuous curve) and by Rae /8/ (dashed curve) for s-triazine.

## 3. DISCUSSION

The specific heat $C_V$ was calculated as a function of temperature using a mean-field model developed by Rae /8/ who calculated the free energy which was also calculated by Ewen and Dove /7/ for the ferro-elastic phase transition in s-triazine, as given in Fig. 2. Using the free energy functional form (Eq. 1) /7/, the temperature dependence of the specific heat $C_V$ was evaluated (Fig. 3) in this study.

When the free energy was calculated by Rae /8/, we used the observed Raman frequencies /14/ which were related to the shear strain angle (order parameter) according to Eq. (2) and it was calculated below $T_C$ down to about 150 K. Similarly, Ewen and Dove /7/ used their observed Raman frequencies for the modes I, II, IV and V, which were also related to the shear strain angle (Eq. 2) to calculate the free energy (Eq. 1) below $T_C$, as shown in Fig. 2. The fitting parameters (Eq. 2) can be compared for both calculations of the free energy (Table 1). As indicated previously /7, 8/, the Raman frequencies of the bands I and II, and of bands IV and V, cross at temperatures below the transition temperature ($T_C$ = 198 K) (Table 1). When compared the free energies, Ewen and Dove /7/ obtained lower values than those obtained by Rae /8/ (Fig. 2). This difference in the free energy may be due to the fact that the Raman frequencies which were related to the order parameter (Eq. 2), were measured by Ewen and Dove closer to the ferro-elastic phase transition, in comparison with those measurements /14/, as also pointed out previously /7/. When the free energy was calculated, it has been reported /7/ that the expression (Eq. 2) for the frequencies of the Raman-active modes (I, II, IV and V) are not valid for large shear strain angle $\Theta$ (order parameter). So, for large order parameter values the frequencies $\omega_0$ and $\omega_0'$ (Table 1) for the high-temperature phase (phase I) of s-triazine is no longer temperature independent. Thus, by expanding the free energy in terms of the order parameter, in other words, by expanding the potential energy of the crystal in terms of the normal-mode coordinates of the Raman-active and soft-acoustic phonon modes, the free energy was calculated /7/. For this expansion, a coupling between the acoustic mode and the optic modes was considered. The frequencies of the Raman-active modes $\omega_I$ , $\omega_{II}$ , $\omega_{IV}$ and $\omega_V$ were then obtained as a function of the order parameter $\Theta$ (Eq. 2). By fitting the observed Raman frequencies of the four Raman-active bands /7/ to the observed shear strain angle $\Theta$ /2, 13/ at various temperatures (Fig. 1), fitted parameters were obtained (Table 1) and they were used in Eq. (4) to evaluate $V(\Theta)$ according to Eq. (3). By establishing the sum over the temperature dependence of the observed Raman modes I, II, IV and V according to the Einstein model in Eq. 1, and $V(\Theta)$ (Eq. 4) where the temperature dependence of $\Theta$ /2, 13/ (Fig. 1) was used, the free energy F was then evaluated as a function of temperature /7/, as given in Fig. 2. The specific heat $C_V$ calculated from the free energy functional (Eq. (1)), as presented in this study (Fig. 3) increases with increasing temperature below $T_C$ for the ferro-elastic phase transition of s-triazine. It was calculated for the nonzero order parameter (shear strain angle) using the observed Raman frequencies of the modes I, II, IV and V, as stated above. So, the specific heat $C_V$ was obtained as a function of temperature below $T_C$ in a large temperature interval from 150 K up to about 200 K, as the free energy was also evaluated (Fig. 2). In comparison with the specific heat $C_P$, close to the transition temperature ($T_C$ =198 K) a sharp peak in $C_P$ occurs which has been observed experimentally in s-triazine /3/, as we have also analyzed its critical behaviour using a power-law formula in our recent study /15/. It was concluded that a rapid rise in the specific heat $C_P$ represents a latent heat associated with the discontinuous change in the shear strain angle $\Theta$ /3/. This was counted by a mean-field model and it was also concluded that the residual specific heat anomaly is due to fluctuations in the order parameter near the transition temperature ($T_C$ = 198 K) for s-triazine, which are not taken into account in the mean field models, as also pointed out previously /3/. Regarding the specific heat $C_V$ calculated here, there is no anomalous behaviour of the specific heat in the vicinity of the transition temperature ($T_C$ = 198 K) as the halfwidth /7/ or the damping constant /11/ in s-triazine. Since the specific heat $C_V$ was calculated from the Raman frequencies of the modes I, II, IV and V, which decrease continuously with increasing temperature towards $T_C$, as observed experimentally /7/, the $C_V$ behaviour suggests that the transition in s-triazine is of a continuous type.

## 4. CONCLUSION

The specific heat $C_V$ was calculated from the free energy expanded in terms of the shear strain angle $\Theta$ (order parameter) which was related to the Raman frequencies of the modes I, II, IV and V of s-triazine below $T_C$. The temperature dependence of the observed Raman frequencies were used in the Einstein model to predict the $C_V$ values within the mean-field model, which increase with increasing temperature towards $T_C$, as expected. This gives a support that the mean-field approach studied here describes the temperature dependence of the specific heat $C_V$ correctly. An Einstein model which takes into account the Raman-active modes (I, II, IV and V) for s-triazine with the mean-field approach as studied here, can be considered for some other crystalline systems treated using the quasi-harmonic approximation.

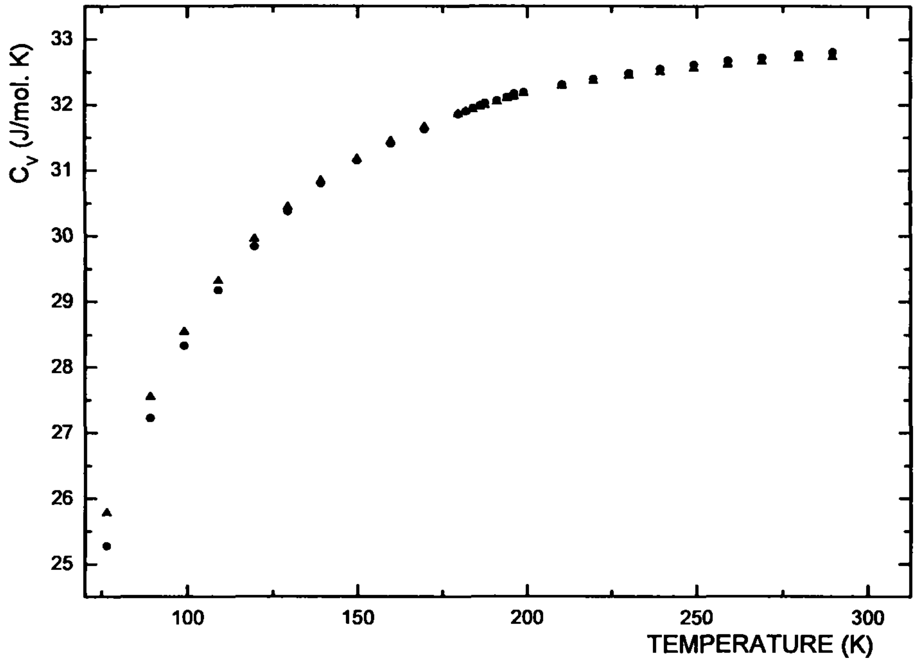

**Fig. 3:** Calculated specific heat $C_V$ as a function of temperature from the free energy (Eq. 1) for the I-II phase transition in s-triazine. ● represents the specific heat $C_V$ calculated using the observed Raman frequencies /7/. ▲ represents the $C_V$ calculated from the Raman frequencies evaluated by Eq. (2) using the $\theta$ values /8/, according to Eq. (1).

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