

A Raman scattering study of the pressure induced phase transition in *s*-triazine

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The pressure induced phase transition in *s*-triazine has been studied using Raman scattering. Some of the features observed in a previous Raman scattering study of the phase transition at atmospheric pressure have also been observed in the present case, and a preliminary analysis based on an estimated form of the pressure dependence of the order parameter is reported. However, the data presented in the present study can not yet be fully reconciled with the corresponding results at atmospheric pressure. It is suggested that some of the different theoretical ideas concerning the transition developed for atmospheric pressure and variable temperature could be applied in the analysis of the effects of pressure. No additional phases of *s*-triazine were observed at pressures up to about 30 kbar within the temperature range 15–295 K.

I. INTRODUCTION

The existence of a weakly first order ferroelastic phase transition in *s*-triazine ($C_3N_3H_3$) has been known for some time. The variation of the crystal structure of the low-temperature low-pressure phase with temperature was determined by Smith and Rae¹ and Prasad *et al.*² The rhombohedral symmetry of the high-temperature low-pressure phase (called phase I) is broken by two principal mechanisms. Firstly, there is a spontaneous shear distortion of the unit cell (θ) to form a monoclinic unit cell on cooling below the phase transition temperature and secondly, there are small symmetry-breaking rotations of the molecules about axes perpendicular to the shear plane (φ). The change in the space group symmetry ($R\bar{3}c$ to $C2/c$, preserving the number of molecules per unit cell) suggests the existence of other symmetry breaking distortions, but these have been shown to be negligibly small in comparison with the unit cell shear and molecular rotations. Rae³ has suggested that the transition should be accompanied by a soft acoustic mode, and this has been observed by coherent inelastic neutron scattering measurements^{4,5} and in Brillouin scattering measurements.⁶ There are no corresponding soft optic modes, but three zone-center optic modes that are degenerate in phase I are split in the low symmetry phase (called phase II). The infrared and Raman spectra of *s*-triazine have been studied in detail by several workers.^{7–9} The present authors also presented a group theoretical analysis of the zone-center lattice modes for phase II.⁹ Other experimental measurements associated with the I–II phase transition in *s*-triazine at low pressures are specific heat calorimetry¹⁰ and nuclear quadrupole resonance,¹¹ the latter results being reconciled with the crystallographic results by Rae.¹²

There have been a number of serious attempts to develop a theoretical understanding of the low-pressure I–II transition in *s*-triazine.^{3,12–16} Through the work of these authors many of the important features of the transition have been identified, but the different approaches have led to

different suggestions concerning the microscopic origin of the phase transition. At the present time it is not possible to distinguish the correctness of the different approaches. In part this is because the ferroelastic phase transition in *s*-triazine is correctly described by mean-field theory so that the different theoretical approaches each indicate only small deviations from standard Landau theory (containing the cubic term in the order parameter; see Ref. 12) and each theory requires a certain measure of phenomenological parameter fitting. The main differences between the various approaches lie in the origin of the temperature dependence in the corresponding Landau theory: Rae¹³ interprets the temperature dependence of the free energy as arising from the density of states of the optic phonons that couple to the soft acoustic mode, with this soft mode having a negligible contribution itself to the free energy, whereas Raich and Bernstein¹⁴ have incorporated temperature into the free energy expansion from a consideration of entropy by assuming that the *s*-triazine molecules are orientationally disordered between equivalent sites related by the molecular twofold axes. Luty and Van der Avoird¹⁶ follow Raich and Bernstein at this point. Thus Rae¹³ suggests that the phase transition is a purely displacive transition with the molecular reorientation in the low symmetry phase II arising as a consequence of a coupling between the soft acoustic mode and the relevant optic modes whose eigenvectors consist of rotations and translations of the molecules, and Raich and Bernstein¹⁴ interpret the transition partly as an order–disorder transition with similarities to a plastic phase transition, with the unit-cell distortion arising as a result of coupling between the orientations and displacements of the molecules. Luty and Van der Avoird¹⁶ take a similar approach to Raich and Bernstein, but differ in that whereas the rotation–translation coupling in Raich and Bernstein's model leads to an indirect orientational interaction, Luty and Van der Avoird suggest that the primary effect of this coupling is an indirect translational interaction.

What the different approaches do have in common is that they stress the importance of coupling between the orientations of the molecules and the acoustic phonons. Thus a full description of the phase transition in *s*-triazine evokes

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concepts that are currently being successfully applied to the analyses of plastic crystal phase transitions¹⁷ in which the onset of orientational order below the transition temperature is accompanied by a ferroelastic distortion of the unit cell. It should however be borne in mind that the molecular motions in *s*-triazine are not nearly as anharmonic in nature as in genuine plastic crystals, and the optic phonons (which have been studied in detail only at the Brillouin zone center and only on a preliminary basis at other points in the Brillouin zone⁵) appear to be relatively well resolved and not overdamped as commonly found in plastic crystals.

A further aspect that is highlighted by a comparison of the different theoretical descriptions of the phase transition in *s*-triazine concerns the definition of the order parameter for the transition. The two main components of the broken symmetry are the shear strain θ (or more correctly $\tan \theta$, but in the small angle limit these two quantities are almost identical) and the molecular rotation angle φ , and the crystallographic studies have shown that these two quantities are not strictly proportional to each other over the full range of measurements below the transition temperature. Therefore only one of these parameters or some functional combination of them can be strictly identified with the order parameter. Rae¹³ has argued on general grounds within the harmonic approximation that in such a transition it will only be the shear strain that is the order parameter, and that the molecular rotation angle is a quadratic function of θ . However, this has been criticized by Luty and Van der Avoird¹⁶ who suggest that the nonlinear relationship is a consequence only of anharmonic effects. Raich and Bernstein^{14,15} have taken both θ and φ to be independent order parameters, but their work has carried out before the nonlinearity was established. In this latter case, φ is presumed to be the correct order parameter for the transition.

The different theoretical approaches might be critically tested by demanding that they be able to describe not just the atmospheric-pressure phase transition but the full pressure-temperature phase diagram. This is particularly true since any theory must be able to describe the pressure induced I-II transition at constant temperature, thereby possibly probing the basis of the different theories.

The pressure-temperature phase diagram has been studied by nuclear quadrupole resonance¹⁸ and by neutron scattering,¹⁹ and is shown in Fig. 1. It can be seen that the transition temperature T_c varies linearly with pressure P (units of kbar) according to the relationship $T_c = 198 + 18.7P$, and that the law of corresponding states, which postulates that the phase behavior can be simply described by the effect of pressure on the transition temperature by assuming that the order parameter is dependent only upon a general reduced temperature $t = [T - T_c(P)]/T_c(P)$, is reasonably well obeyed close to the transition line. The neutron scattering study also showed that the soft acoustic phonon associated with the I-II transition at low pressure also softens on approaching the pressure induced transition at room temperature. However, in order to quantitatively analyze the full phase diagram many more high pressure measurements are required. Thus the purpose of the present paper is to present the results of a study of the

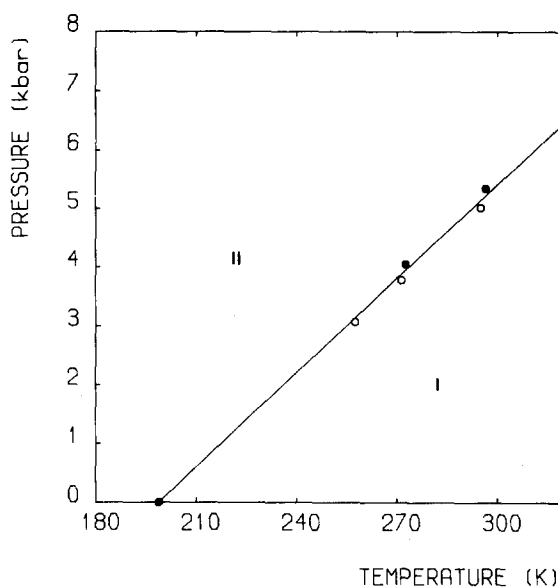


FIG. 1. The phase diagram of *s*-triazine. The open and filled circles correspond to transition points located by neutron diffraction (Ref. 19) and nqr (Ref. 18), respectively. Phases I and II are the rhombohedral and monoclinic phases, respectively.

Raman spectrum of *s*-triazine at high pressures. We plan a crystallographic study of the pressure induced transition at a later date. It is hoped that a full understanding of the phase behavior of *s*-triazine with the resolution of the different interpretations will lead to a better understanding of many other systems as many of the points and questions raised by some of the authors cited above appear to have a more general relevance.

In addition to a consideration of the above issues we also sought to make an exploratory investigation of the full phase diagram of *s*-triazine in the region $15 < T < 295$ K and $0 < P < 30$ kbar in order to find whether or not there are any other structural phase transitions in addition to the one discussed above. As will be shown later, this search showed that within the limits of the phase diagram studied, the only stable phases are phases I and II.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of *s*-triazine (obtained from Aldrich Chemical Company) were used as supplied: Raman spectra recorded at room temperature and atmospheric pressure were in agreement with those obtained in previous studies and showed no evidence of impurities or polymerization. Pressure was applied by means of a diamond anvil cell (purpose built by Diacell Products²⁰) the *s*-triazine being contained in a 0.2–0.3 mm diameter hole spark-etched in an "inconel" or phosphor-bronze gasket. Pressure was measured by monitoring the *R* lines in the fluorescence spectrum of a 20 μ m chip of natural ruby included with the sample, the *R* line shift being taken as $-0.76 \text{ cm}^{-1} \text{ kbar}^{-1}$.²¹ The complete fluorescence spectrum over the range 14 350–14 450 cm^{-1} was recorded at each pressure so that the frequencies and widths of both the *R* lines could be monitored: no indication of significant pressure gradients was observed. The spread in Raman frequencies as a function of pressure (see Fig. 4) is consistent with an error of ± 0.5 kbar in the pres-

sure values, which is expected for this technique.²²

High pressure Raman spectra at low temperatures were obtained by mounting the pressure cell on the tail of a CT1 21SC cryogenic refrigerator. The absolute sample temperature (correct to ± 5 K) was determined using a Si diode mounted on the cell and checked by measuring the intensity ratio of Stokes and anti-Stokes spectra. The shift in the *R* line frequencies as a function of decreasing temperature (at atmospheric pressure) was measured in a separate experiment and used in determining the sample pressure at low temperatures: the *R* line shift with pressure was taken to be independent of temperature.²³

Raman spectra were excited with 100 mW or less of 530.9 nm light from a krypton ion laser, the beam being passed through a single stage monochromator to remove plasma lines. A microcomputer controlled Coderg T800 triple spectrometer was used to record the spectra, which was obtained with a backscattering configuration. The slitwidths were set to give a resolution of 2.25 cm^{-1} . The error in the Raman frequencies is less than $\pm 0.5 \text{ cm}^{-1}$.

III. RESULTS

Representative Raman spectra of *s*-triazine over the range $0\text{--}750 \text{ cm}^{-1}$ are shown for various pressures in Fig. 2. For clarity the spectra have been displaced diagonally, each spectrum having been shifted vertically and translated by 40 cm^{-1} relative to the one beneath. The bands at 340 and 675 cm^{-1} are the lowest frequency internal modes observable, while those below 200 cm^{-1} are the external (lattice) modes. The spectra are normalized to the intensity of the 675 cm^{-1} bands.

The intensities of all the lattice modes decrease dramatically with pressure. This is presumably due to the fact that the volume changes that are associated with the increased pressure reduce the amplitudes of molecular vibra-

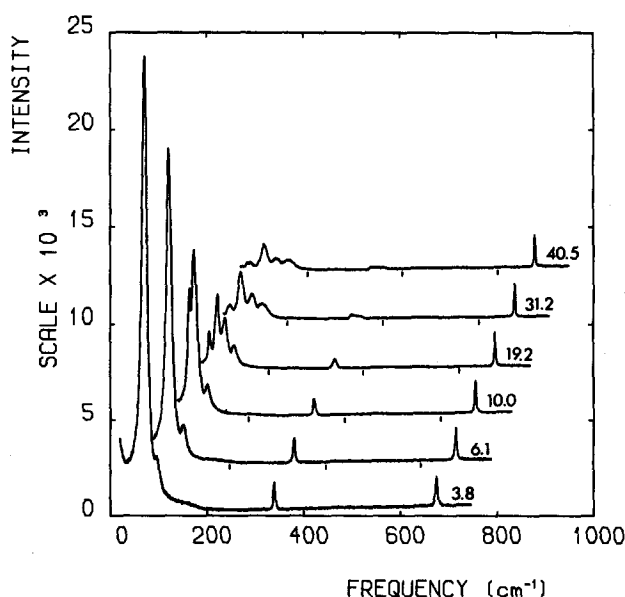


FIG. 2. Raman spectra of *s*-triazine at different pressures at room temperature. The spectra have been normalized to the intensity of the internal band at 675 cm^{-1} . Values on spectra are in kbar, and the horizontal axes of sequential spectra are displaced by 40 cm^{-1} .

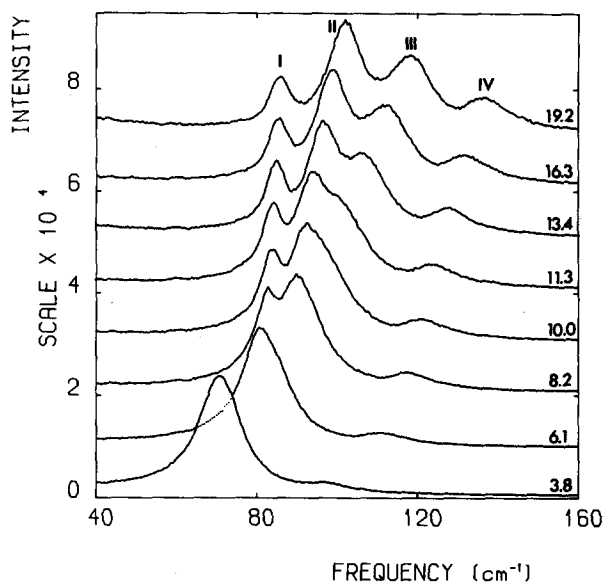


FIG. 3. The lattice mode region of the Raman spectrum of *s*-triazine at different pressures normalized to the most intense peak. Values on spectra are in kbar. The bands are labeled as described in the text.

tions. There are also changes in the intensities of the external modes relative to each other: these will be discussed later.

Two other points are worth noting in Fig. 2. First, as the pressure increases, the lowest frequency internal mode at 340 cm^{-1} weakens, broadens, and eventually splits. This band is doubly degenerate (E_g) in phase I and is expected to split in phase II; no corresponding splitting is observed in the low temperature, atmospheric pressure results.⁷ Secondly, there is a broad weak feature between 120 and 200 cm^{-1} . Although it appears to vanish as the pressure is increased this may be due to it becoming undetectable as a result of the general decrease in intensity in the low frequency region of the spectrum. We have also observed this feature in the room temperature atmospheric pressure spectrum, and we attribute it to second-order processes.

The changes occurring in the external modes are more clearly seen in Fig. 3, which shows the $40\text{--}160 \text{ cm}^{-1}$ region of a number of spectra at various pressures up to 19.2 kbar . The spectra are normalized by maximum intensity and for clarity have been vertically (but not horizontally) displaced. The external bands have been labeled I–IV in a manner similar to the labeling of the modes at atmospheric pressure⁹ but without definitely identifying correspondences (see below). The changes in the peak positions are the actual pressure induced shifts. The phase I spectrum (3.8 kbar) contains two bands, both of E_g symmetry. With increasing pressure the main band splits into two and a fourth band emerges between it and the highest frequency band, which itself does not change significantly. All the external bands move steadily to higher frequencies as the pressure increases. The group theory analysis of the phase transition presented earlier⁹ predicts that the transition from phase I to phase II should cause the two E_g modes in the Raman spectrum to split and should activate the two silent A_{2g} modes, giving a total of six bands in the external spectrum of phase II. Although six bands have been located for phase II in the low temperature atmospheric pressure spectra they are not always all resolvable.

ble, due to temperature broadening, overlap of bands and low relative intensities of some bands. In the present case one would expect to see the highest frequency band split into two with a sixth band emerging in its vicinity. It appears that these two additional bands are either too weak to be detected or else overlap the stronger bands at lower frequencies. In the case of the split component, the splitting may be too small to be resolved. This possibility has been suggested by Luty and Van der Avoird¹⁶ on the basis of their calculations of phonon dispersion curves for the two phases.

Figure 4 shows the variation of frequency with pressure for the external bands, and the data are given in Table I. There is a discontinuity between the frequencies of the E_g modes of phase I and of the corresponding A_g and B_g modes of phase II at the expected transition pressure ($P_c = 4$ kbar), although it is much larger than at the transition point at atmospheric pressure on cooling. For pressures just above P_c bands I, II, and III are not all resolved, as Fig. 3 shows, and the spectra had to be fitted with Lorentzian line shapes in order to obtain the peak frequencies as in our previous study of the Raman spectrum of *s*-triazine.⁹ Those frequencies that have been determined from such fits are represented by triangles. The solid lines show a theoretical variation of frequency with pressure for bands I and II and will be discussed in Sec. IV.

As well as the overall decrease in intensity of the external bands relative to the internal bands, there are changes in the intensities of the four external bands observed above P_c relative to each other. The variation with pressure of the intensities of bands I–III relative to band IV is shown in Fig. 5. To take into account the background and overlapping of bands the spectra were fitted with Lorentzian line shapes and the fitted peak intensities were used rather than those measured directly. For each spectrum the fitted intensities of bands I–III were divided by that for band IV to obtain the relative intensities. The intensity of band I decreases rapidly

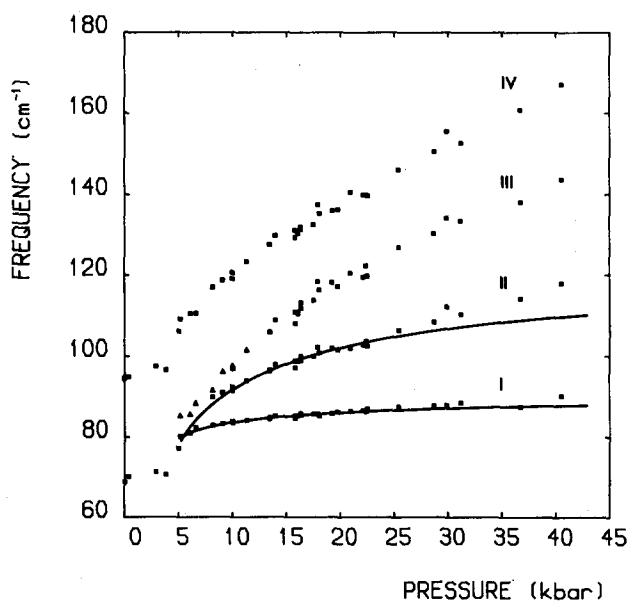


FIG. 4. The frequencies of the resolvable lattice modes of *s*-triazine as a function of pressure. The triangles represent those data that were obtained from least squares fitting of Lorentzian line shapes to the spectra, and the solid curves are the result of a calculation described in the text.

TABLE I. Pressures and Raman frequencies for the data points of Fig. 4. Frequencies marked * were obtained from least squares fits to the spectra. Columns I–IV refer to the corresponding bands of phase II. The pressures are correct to ± 0.5 kbar and the frequencies to ± 0.5 cm^{-1} .

Pressure (kbar)	Frequencies (cm^{-1})				
	I	II	III	IV	
0.0	68.9			94.4	Phase I
0.4	70.3			94.9	
2.9	71.5			97.5	
3.8	70.8			96.6	
5.0	77.3			106.1	
	I	II	III	IV	
5.1	80.2		85.4*	109.1	Phase II
6.1	81.0		85.7*	110.5	
6.6	82.3		88.4*	110.6	
8.2	82.9	89.9	91.6*	117.0	
9.1	83.3	91.0	96.2*	118.7	
10.0	83.5	91.5	97.0*	119.1	
10.0	83.9	92.4	97.7*	120.6	
11.3	84.1	93.9	101.6*	123.3	
13.4	84.5	96.3	105.9	127.5	
13.4	84.8	96.6	106.0	127.6	
14.0	85.2	97.9	108.9	129.8	
15.8	84.6	97.1	108.1	129.3	
15.8	85.3	98.8	110.9	131.3	
16.1	85.3	98.7	110.5	130.3	
16.3	85.4	98.9	111.8	131.3	
16.3	85.8	99.9	113.2	131.9	
17.5	85.7	100.0	113.8	132.5	
17.9	85.7	102.2	118.4	137.5	
18.0	85.2	100.8	116.3	135.3	
19.2	85.8	102.0	118.2	136.0	
19.7	86.2	101.5	117.1	136.2	
20.9	86.4	102.0	120.5	140.6	
22.1	86.6	102.8	119.5	139.9	
22.4	86.3	103.7	122.3	139.9	
22.5	86.9	102.5	119.8	139.7	
25.4	87.5	106.4	126.9	146.2	
28.7	87.8	108.5	130.3	150.6	
29.9	87.9	112.2	134.1	155.5	
31.2	88.5	110.4	133.5	152.7	
36.7	87.4	114.2	138.1	160.8	
40.5	90.2	118.0	143.8	167.1	

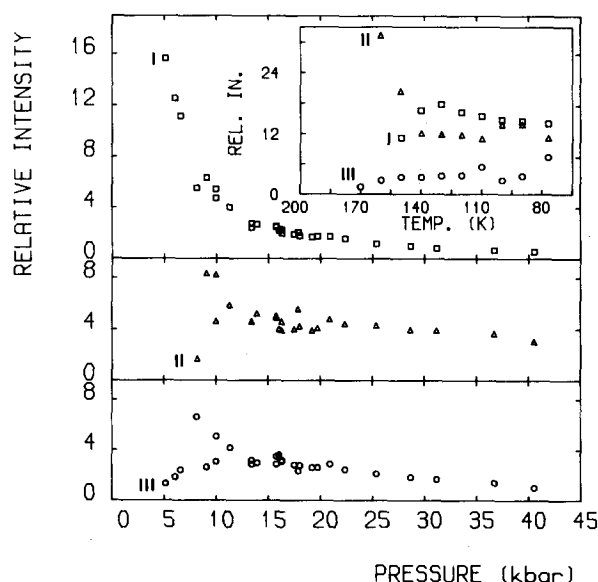


FIG. 5. Intensities of the three lowest frequency lattice modes as functions of pressure and temperature (insert).

with increasing pressure whereas bands II and III increase from atmospheric pressure to a maximum at 8–9 kbar and then decrease gradually. The large fluctuations in the intensities of bands II and III in the region of 8–10 kbar may be due to the frequencies of bands II and III being very close at this point. For comparison, the inset of Fig. 5 shows the variation of relative intensity with decreasing temperature at atmospheric pressure, the results being taken from our previous study (Ref. 9, the actual figures are unpublished). The data, which again were derived from sets of Lorentzian line shapes fitted to the measured spectra, were corrected for the Bose–Einstein temperature factor and normalized to the intensity of peak IV. (Note that in the high pressure spectra band IV is probably an unresolved doublet corresponding to bands IV and V of the previous study.⁹) As in the pressure case, one of the bands is intense close to the transition point, with the other two bands having extremely low intensities that increase on moving away from the transition point into phase II. However, the correspondence between the behavior in the two cases is not fully understood, as will be discussed later.

Figure 6 compares the lattice mode regions of the high pressure Raman spectra of *s*-triazine at room temperature and 15 K. The 15 K spectrum is in fact considerably weaker but has been scaled to equalize the intensities of band II. The weakness of the low temperature spectrum makes the background on which it is superimposed more noticeable; this background is partly due to the exciting line and partly due to fluorescence originating from the components of the diamond anvil cell. The four bands of the room temperature 40.5 kbar spectrum are still observable in the 15 K, 29.3 kbar spectrum although they have been shifted to higher frequencies and have undergone changes in relative intensity. The peak frequencies for the four bands are indicated in Fig. 6.

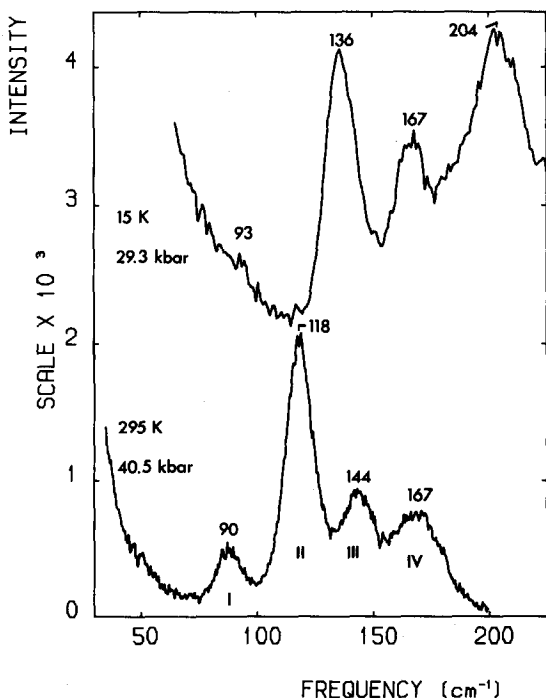


FIG. 6. High pressure Raman spectra of *s*-triazine at two different temperatures. The peak frequencies of the bands (in cm^{-1}) are indicated.

There is no evidence in the lattice mode region of any additional structural phase transitions at high pressures and low temperatures.

IV. DISCUSSION

As stated in the Introduction, a full analysis of the pressure induced phase transition in *s*-triazine will require an extensive set of different experimental results, particularly crystallographic results, which are not yet available. However, in order to provide a preliminary assessment of the data reported here we have needed to estimate the form of the variation of the order parameter (taken to be the shear strain θ) with pressure. The previous nqr¹⁸ and neutron scattering¹⁹ studies of the pressure induced transition indicate that close to the transition the variation of the order parameter can be described by assuming that θ is a function only of the reduced temperature as given in the Introduction, with the effects of temperature (T) and pressure (P) being subsumed in the dependence of the reduced temperature $t(T, P)$ on these quantities. The main difficulty with this approach is that the first order nature of the transition implies some ambiguity in whether one uses the transition temperature or the temperature at which the free energy at $\theta = 0$ changes from a minimum to a maximum (see Ref. 1 for the relation between these two temperatures). However, because the transition in *s*-triazine is only weakly first order, the computed values of the order parameter at high pressures using the two temperatures do not differ significantly, and we have taken the transition temperature as the appropriate temperature to use in the evaluation of t . The validity of the reduced temperature approach has been tested for $0 < t < 0.03$ by nqr,¹⁸ and the results confirmed over one half of this range by a neutron scattering determination of $\theta(P)$.¹⁹ The nqr analysis is slightly misleading since the measured nqr line splittings were erroneously taken to be proportional to the order parameter (Rae¹² has shown that the line splittings in fact have a quadratic dependence on θ) but the conclusions regarding the range of validity of the reduced temperature approach remain intact. It is not clear that the reduced temperature approach is valid outside of this range, but the variation of θ with t is much more gradual at larger values of t so that departures from this approach will be expected to be minimized.

In our estimate of the pressure dependence of θ we follow the reduced temperature approach and take θ to be a simple function of t , and obtain values of $\theta(P)$ from $\theta(T)$ at atmospheric pressure. In fact, rather than use the straightforward data of Ref. 1, we used values for $\theta(T)$ as calculated from Landau theory presented in Ref. 1. The reason for this is as follows: The maximum value of P of 40.2 kbar used in the present study corresponds to $t = 0.69$, which is equivalent to a temperature of 62 K at atmospheric pressure. It is clear from the results of Ref. 1 that Landau theory gives a good quantitative description of the variation of θ with T , and the discrepancies at low temperatures can be attributed to the fact that Landau theory is intrinsically incorrect in the limit $T \rightarrow 0$.¹³ Thus the experimental data will contain the effects of approaching 0 K which are inappropriate for the analysis of data for variable pressure at constant tempera-

tures, and this is why we chose to use the results of Landau theory rather than the pure experimental results. It should be noted however that the differences between the experimental and calculated values of θ differ by 12% at most over the range of t used in the present study.

Rae¹³ has proposed that in phase II the frequencies of the modes that are degenerate in phase I can be expressed as functions of θ in the form

$$\omega_{\text{I}}^2 = \omega_0^2 + \alpha\theta + \beta_1\theta^2,$$

$$\omega_{\text{II}}^2 = \omega_0^2 - \alpha\theta + \beta_2\theta^2,$$

with corresponding forms of these equations for bands IV and V, which are not resolvable in the present study, and for two bands that are infrared active and which are degenerate in phase I. In the case of variable temperature at atmospheric pressure, the relative magnitudes of the parameters in the above expressions result in the frequencies of the corresponding bands crossing just below the transition temperature,^{9,13} and it is of interest to see whether this kind of behavior also exists in the present case. In Fig. 7 we present a fit of this function to the experimental data for the frequencies of band I and II (which we have taken to be the two bands that are degenerate in phase I) and the estimated form of $\theta(P)$ and the resultant computed variation of the frequencies with pressure are shown as the solid lines in Fig. 4. The fitted parameters are given in Table II, and compared with the corresponding results for the atmospheric pressure data obtained previously by the present authors.⁹ It can be seen that the values of the parameters for the constant pressure and temperature cases are fairly close, which is the *a posteriori* justification for assigning bands I and II as the pair that are degenerate in phase I, and that as in the atmospheric pressure case the frequencies of these two bands do indeed cross. Although it is clear that this fitting procedure is partly speculative at the present time, if the reader is prepared to accept that the estimated form of $\theta(P)$ is likely to be in reasonable

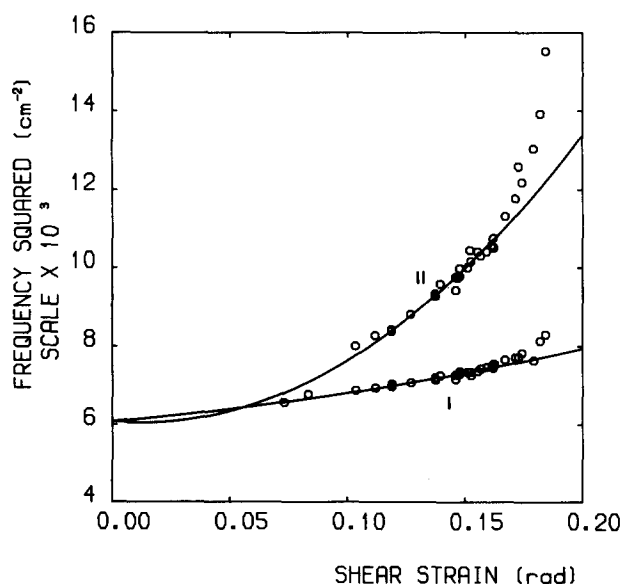


FIG. 7. Squares of the frequencies of lattice modes I and II as functions of the estimated shear strain in phase II. The solid curves are the result of a calculation, and the parameters used are given in Table II.

TABLE II. Values of the coefficients in the expressions for the frequencies of the split Raman bands. Column A corresponds to the present measurements at $T = 295$ K, and column B to measurements at atmospheric pressure taken from Ref. 9.

	A	B
ω_0^2	6 084	5 314 cm ⁻²
α	5 222	3 700 cm ⁻² rad ⁻¹
β_1	20 306	20 800 cm ⁻² rad ⁻²
β_2	208 705	101 000 cm ⁻² rad ⁻²

agreement with the true form of $\theta(P)$, then it is also reasonable to suppose that the above expressions for $\omega(\theta)$ will also be good descriptions of the true behavior. We plan to measure the crystallographic properties of *s*-triazine at high pressures using neutron powder diffraction in the near future, when we will then be able to reanalyze the present data on a more quantitative basis. It might be expected that the present data could be used to yield information concerning the nature of higher order contributions to the expansion of the lattice frequencies (and hence also the orientational potential seen by the *s*-triazine molecules) in terms of the order parameter.

Also of interest is the variation of the intensities of the Raman bands with pressure in the vicinity of the phase transition. It appears that when the low frequency E_g mode splits at the I–II transition, one of the components has a very low intensity compared to the other one, which increases gradually on moving away from the transition point. This feature has been observed in both the results at atmospheric pressure with variable T ⁹ and now at constant T with variable P , both sets of results acting to confirm the other. However, the picture is not quite as simple if we take the correspondence between the Raman bands of phase II for the two sets of data obtained (at constant T and constant P) that has been assumed in the previous discussion on the pressure (or order parameter) dependence of the frequencies of the lattice modes. In both cases the intensity of band III decreases to zero on approaching the transition line from phase II as expected, but in the case of the doublet that forms the degenerate E_g mode in phase I, it is the intensity of band I that falls to zero on approaching the transition point in the constant T case, but the intensity of band II that falls to zero in the constant P measurements.

In any case, it is not at all clear why the intensities of either bands I or II should fall to zero at a transition point at all. If we consider a harmonic picture, then in the limit that $\{\theta, \varphi\} \rightarrow 0$ the eigenvector of one of the two bands that are degenerate in phase I consists of rotations about the molecular twofold axis and translations along that axis, and the other eigenvector of corresponding motions about and along an axis orthogonal to the molecular twofold axis lying in the molecular plane,^{9,16} with the two modes having equal ratios of rotational and translational motions. We might expect that this picture would be only slightly modified in the presence of the ferroelastic distortion, so that the intensities of the two bands would be nearly equal. In fact, the two intensities are similar far away from the transition point (see Fig. 5 and Ref. 9). In the harmonic picture, these two bands in phase II are not allowed to interact, being of different sym-

metry types, but there might be some mixing of the eigenvector of the B_g component with that of band III, which is also of symmetry B_g . However, if there is in practice significant mixing of these two eigenvectors, it would be expected that the intensity of band III would be stronger at the transition point than is observed.

The most likely explanation for this intensity behavior is that the eigenvectors of modes I and II are modified by anharmonic interactions so that one mode becomes primarily rotational (the more intense band) and the other primarily translational.⁹ It is possible that the largest anharmonic interactions are between modes I and II themselves, particularly since the frequency cross-over behavior that has been observed means that the frequencies of these two modes are very close over a wide range of temperature and pressure. When the frequencies of these two bands do separate, the anharmonic interactions might weaken and the harmonic description outlined above become a more accurate picture. This is consistent with the intensities of bands I and II becoming closer at high pressures and at low temperatures. The nature of these anharmonicities and their influence on the eigenvectors of the modes in phase II remain to be identified and understood, and presumably also do the roles of temperature and pressure since which particular band has low intensity appears to be dependent on the location in the P - T phase diagram. We would like to remark on the fact that in a full theoretical description of the phase transition in s -triazine these features should be taken into account since the eigenvectors of the optic modes do appear to play a significant role in the nature of the transition via their coupling to the soft acoustic mode. Thus it might be expected that the constants in the expressions for the order parameter dependence of the optic mode frequencies given above might themselves be dependent on the order parameter.

V. CONCLUSIONS

It is clear that the results at constant T do not simply mirror those at constant P , at least in the range of measurements reported here and in Ref. 9. The differences that have emerged are associated with the properties of bands I-III. One might expect on the basis of previous high pressure measurements^{18,19} that the principle features of the I-II transition in s -triazine should be relatively unaffected by the location of the transition point along the transition line in the P - T phase diagram (see Fig. 1). However, the present study has shown that although the features of the Raman spectra in the vicinities of the transition line are similar at different points along the line, there are significant differences. If we conclude that the order parameter dependence of the frequencies of the Raman bands is similar in the two cases now studied (constant T and constant P) then the intensity data are "apparently" inconsistent between the two data sets. But if on the other hand we demand that the intensity data be consistent, then there is no relationship between the frequencies of the Raman bands in phase II that is approximately independent of the location in the P - T phase diagram, and the good agreement between the two sets of figures in Table

II is purely coincidental. This condition may not be critical as far as band III is concerned, but one might expect that the relative frequencies of bands I and II might be maintained.

In the Introduction we suggested that the theoretical ideas that have been developed by different authors should be applied to obtaining a description of the pressure induced phase transition in s -triazine. So far, different theories have focused on predicting the temperature dependence of various critical quantities such as order parameter and the velocity of sound associated with the soft acoustic mode. In addition, it would be worthwhile calculating the temperature and pressure dependencies of other quantities such as the relative intensities of the external Raman bands, as described above. In general, the first approach of any theory would be to assume that any pressure or temperature dependence of quantities such as the phonon frequencies arise solely from couplings to certain critical quantities such as the order parameter. In practice this will not be the case, and in this connection it is clear from Fig. 4 that the Raman frequencies have a strong pressure dependence that is not connected with the phase transition. Any model should now take account of this.

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