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Light scattering study of the phase transition in *sym*-triazine[a)]

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The ferroelastic phase transition in *sym*-triazine $C_3N_3H_3$ has been investigated by means of Brillouin scattering and correlation spectroscopy. Soft TA modes are observed by Brillouin scattering but a well-defined central peak could not be found. Near the transition in the high temperature phase a 50% increase in Rayleigh intensity is found. No correlation function was observed in the time domain between 1 and 10^{-6} s. These results are discussed by a Landau mean field theory and dynamical rotation–translation coupling theory.

I. INTRODUCTION

Sym-triazine ($C_3N_3H_3$) is a ferroelastic molecular crystal which has been extensively investigated using a variety of experimental techniques.[1–7] The crystal exhibits a temperature/pressure-induced structural phase transition. The high-temperature (low-pressure) averaged structure is $D_{3d}^5(R\bar{3}c)$ and the low-temperature (high-pressure) one is $C_{2h}^6(C2/c)$. A threefold symmetry axis is lost at the transition temperature (~ 198 K), but the size of the unit cell, which contains two molecules, is unchanged. Therefore, the phase transition takes place at the Brillouin zone center (the lattice translation symmetry does not change) and the order parameter is some physical quantity which is transformed according to the E_g irreducible representation of D_{3d}. Basis functions for this irreducible representation are rotations (R_x, R_y) and strains (e_4, e_5) and $(e_6, (e_1-e_2)=e_7)$. Although soft Raman and/or soft acoustic modes can be expected from symmetry arguments, no soft E_g-Raman mode has been observed. Some internal and optical lattice modes do split below the transition temperature, however. Brillouin scattering and acoustic measurements have not been previously reported.

Recently, a neutron inelastic scattering experiment[7] has revealed soft acoustic phonon modes $[001]_{TA}$ and $[100]_{TA}$ around the Brillouin zone center. The elastic constant which is responsible for these soft TA phonons is c_{44} and the phase transition is confirmed as generated by the c_{44} instability.

Raich and Bernstein[8] developed a Landau mean field description of this phase transition. The theory predicts a first order transition due to cubic invariants in the free energy expansion and generates the experimentally established c_{44} instability. In addition, the theory quantitatively accounts for the temperature dependence of the e_5 strain and optical phonon mode splitting. This theory has also been successfully applied to a similar ferroelectric–ferroelastic transition in benzil.[9]

Raich *et al.*[10] extended the mean field theory, using Green's function techniques, to include dynamics of the phase transition and were able to explain the dynamical structure factor observed in the neutron inelastic scattering experiment. Their discussion is essentially similar to that presented for "spin–phonon coupled" systems such as the ammonium halides[11] and "translation–rotation coupled" systems such as alkali cyanides.[12]

The theory of spin–phonon coupled systems predicts two extreme cases depending on the spin relaxation time and the phonon frequency: the "slow relaxation" case, in which a central peak but no soft phonon is expected (NH_4Br)[13]; and the "fast relaxation" case, in which a soft phonon but no central peak near the zone center is expected (KCN).[14] The neutron inelastic scattering experiment[7] suggests the fast relaxation case for triazine, as soft acoustic modes but no central peak are observed.

Brillouin scattering is a powerful technique for the investigation of the dynamics of structural phase transitions and has been applied to many types of systems.[15] Especially for feroelastic crystals undergoing phase transitions, soft acoustic modes and central peaks can be directly observable in the light scattering spectrum. This is the first report of soft acoustic modes in *sym*-triazine observed by the light scattering technique. The results will be discussed employing the theories developed by Raich *et al.*[8,10]

II. EXPERIMENTAL

Sym-triazine has a high vapor pressure and sublimes readily at room temperature. Accordingly, crystals must be grown and handled in sealed tubes. Details of our sample purification and handling methods have been previously reported.[16] The slow sublimation method was applied to grow single crystals in sealed tubes whose dimensions are about $7\times7\times25$ mm^3.

Although the obtained crystals are of high optical quality (an intensity ratio of $I_R/I_B \sim 5$ to 10 was obtained for those samples without any index matching liquid) they are randomly oriented with respect to the glass cell. For the study of phase transitions by Brillouin scattering, well-oriented samples are necessary if the experimentally observed elastic modes are to correspond to fundamental elastic constant expressions of known and simple form. After a large number of attempts, a sample with the expected unique soft mode behavior was obtained and characterized.

The orientation of this crystal was examined by the

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back Laue x-ray method and by polarizing microscope techniques. Unfortunately, the Laue method did not show any pattern, most likely due to the 2 mm of Pyrex the beams had to transverse. By observing birefringence expected for *sym*-triazine, only the threefold axis (chosen as the *c* axis) could be determined. The unique axis of this particular crystal is slightly tilted (~5°) from the long crystal axis in the sample cell. Optical methods could not determine the other two axes.

After location and orientation determination of a good part of this crystal, the sample was extensively investigated and taken through the phase transitions in three separate experiments. Although visible damage is not observed in the sample, the intensity ratio I_R/I_B increased after each run.

Brillouin scattering apparatus including cryogenic and temperature control has been discussed previously.[9] For this experiment, a calibrated copper-constantan thermocouple is placed on the glass sample cell inside the copper cell to improve temperature measurement. The thermocouple voltage is read by a digital multimeter with 1 μV resolution. Temperature of the copper cell is controlled by a proportional controller with a calibrated diode sensor; temperature fluctuation at the sample is less than $\pm 1\ \mu$V (± 0.03 °C) for a data accumulation time of 30 min.

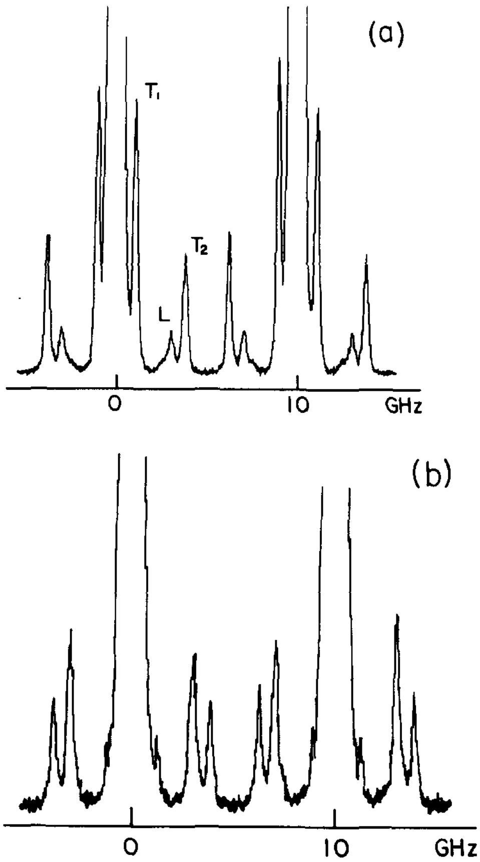

FIG. 1. Brillouin spectra of *sym*-triazine at 197.2 K (T_c+0.1 K). T_1 denotes the main soft transverse acoustic mode associated with c_{44}, T_2 the other soft transverse mode associated with c_{66} and L the longitudinal mode: (a) unpolarized ($H_H + V_H$); (b) polarized H_H. The scattering plane in the *ab* plane.

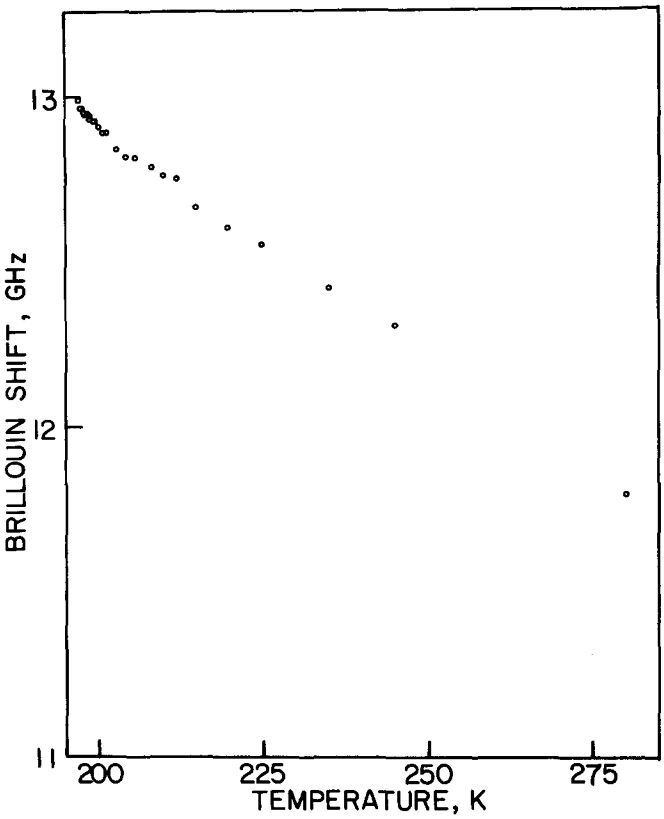

FIG. 2. Temperature dependence of the quasilongitudinal phonon frequency. Same orientation as in Fig. 1.

The free spectral range of the Fabry–Perot interferometer is set to 10 GHz for the soft mode study and 37.5 GHz for peak assignment. The accumulated Brillouin spectra are stored in the memory of a multichannel analyzer and are then transferred to a computer for further calculations. Polarization relations for the Brillouin spectra are examined at room temperature and just above the transition temperature (T_c+0.1 K).

Correlation spectroscopy, using a computer controlled real time correlator which covers the time domain between 1.0 and 10^{-6} s, is simultaneously done with the Brillouin spectroscopy. The details of this combined correlation–Brillouin light scattering apparatus will be presented at a later time.

III. RESULTS

Brillouin spectra obtained at T_c+0.1 K are shown in Fig. 1. Figure 1(a) shows unpolarized H_H + V_H and Fig. 1(b) shows polarized H_H spectra. The soft phonon is completely depolarized, the LA phonon is polarized, and another TA phonon is almost completely depolarized.

Just below the transition temperature T_c = 197.1 K, the Rayleigh intensity suddenly increases and masks the phonon peaks. This is due to domain scattering associated with the first-order nature of this phase transition; accordingly, only the high temperature phase could be systematically investigated.

The LA-phonon frequency monotonically increases as temperature approaches the transition temperature as shown in Fig. 2. In contrast to the LA phonon, two TA phonons decrease in frequency with decreasing temperature in the high temperature phase. The higher frequency phonon decreases in frequency about 15% between room temperature and the transition temperature. On the other hand, the lower frequency TA phonon, the expected soft mode, decreases in frequency over this temperature range by over 60% as shown in Fig. 3.

After the second run, the crystal was rotated 90° in the scattering plane (almost the *ab* plane) and cooled again. A soft mode was also observed even in this orientation and its frequency was slightly higher ($\simeq 2\%-3\%$) than that of the former geometry; this difference is, however, very close to the experimental error for the soft mode frequency ($\simeq \pm 2\%$).

Half-widths of these acoustic phonons are almost the same as the instrumental width ($\simeq 200$ MHz) through the examined temperature range and no anomalous linewidth behavior is observed.

As the precise values of the refractive indices are unknown at present, we can only calculate normalized elastic constants assuming that the refractive indices can be regarded as temperature independent constants. Both of the transverse elastic constants were normalized at 295 K. If the constants are fitted to the theoretical prediction[8]

$$c(T) = C_0 \frac{T - T_1}{T - T_0},$$

in which $T_0 = -759$ K, the obtained parameters are

$$c_{T_1} = 9.16 \frac{T - 180}{T + 759} \quad \text{and} \quad c_{T_2} = 3.80 \frac{T - 17}{T + 759}.$$

The excellent agreement between theory and experiment is depicted in Fig. 4.

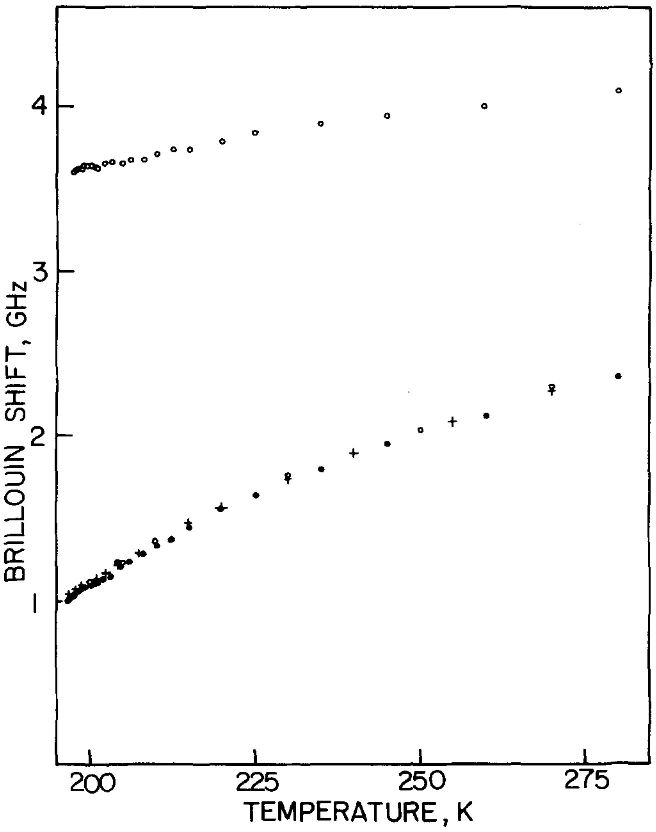

FIG. 3. Temperature dependence of the soft modes T_1 and T_2. Data are plotted for three separate runs, the last of which (+) is for the 90° rotated geometry, in the *ab* plane.

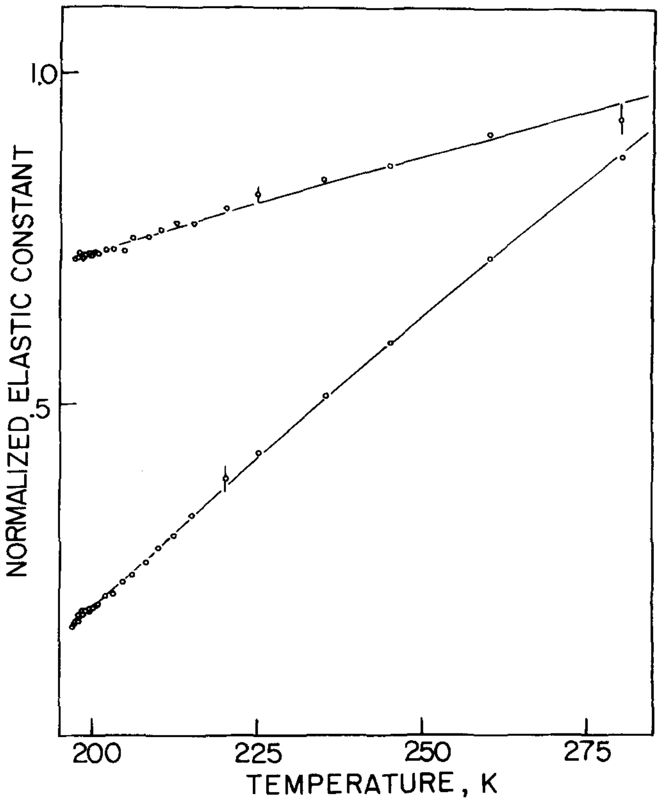

FIG. 4. Temperature dependences of normalized elastic constants are shown for the first run. Normalization temperature is 295 K.

Rayleigh intensity and the intensity ratio of the Rayleigh component and the soft mode were measured for the initial run. These results are shown in Fig. 5. Rayleigh intensity gradually increases as temperature approaches the transition point while the Rayleigh/Brillouin ratio decreases. Therefore, the soft mode intensity increases much faster than the Rayleigh intensity does near the transition temperature. For the second run, these features became less pronounced due to internal fractures introduced at the phase transition.

Correlation spectroscopy was also tried simultaneously with the Brillouin measurements. No correlation function is observed in the time domain between 1 and 10^{-6} s even near the transition temperature.

IV. DISCUSSION

The neutron scattering experiment[7] reveals soft TA phonons whose softening extends considerably into the Brillouin zone. The soft modes are well defined (underdamped) even near the transition temperature and no "central component" was observed in the response function. This gives important information on the dynamics of the phase transition, as discussed in detail below.

The presentation will be divided into two sections. The first will deal with the Landau mean field theory of the soft mode behavior in the high-temperature phase as the transition is approached. The second section will present a general discussion of the dynamical aspects of the phase transition induced through rotation-transition coupling and fluctuations.

A. Soft mode behavior

For the Landau mean field treatment of the phase transition[8] the order parameter has been taken as a doubly degenerate molecular rotation (R_x, R_y) belonging to the E_g irreducible representation of D_{3d}. There are, of course, other sets of basis functions for this representation: strains (e_4, e_5), $(e_6, e_7 = e_1 - e_2)$, and higher-order rotations $(R_x R_y, R_x^2 - R_y^2)$. Because of the expected bilinear coupling between these physical quantities, the choice of order parameter is not unique. The discussion below follows the published theoretical description. As a consequence of cubic invariants of the order parameter in the free energy, theory predicts a first-order transition for *sym*-triazine and a first-order transition is observed experimentally. Below, attention will be focused on elastic anomalies in the high temperature phase.

The free energy for *sym*-triazine is given by[8]

$$F = \tfrac{1}{2}a_0(T - T_0)(R_x^2 + R_y^2) + \tfrac{1}{3}b(R_y^3 - 3R_x^2 R_y) + \tfrac{1}{4}c(R_x^2 + R_y^2)^2 + \frac{1}{2}\,\frac{c_{11}^0 + c_{12}^0}{2}(e_1 + e_2)^2 + \tfrac{1}{2}c_{33}^0 e_3^2 + \tfrac{1}{2}c_{44}^0(e_4^2 + e_5^2) + \frac{1}{2}\,\frac{c_{11}^0 - c_{12}^0}{2}(e_6^2 + e_7^2)$$

$$+ c_{14}^0(e_5 e_7 - e_4 e_6) + A(e_4 R_x - e_5 R_y) + B(e_6 R_x + e_7 R_y) + C\left(e_4 R_x R_y - e_5 \frac{R_x^2 - R_y^2}{2}\right) + D\left(e_6 R_x R_y + e_7\, \frac{R_x^2 - R_y^2}{2}\right) + \cdots . \qquad (1)$$

At the phase transition (below T_c), the crystal develops three domains, "triple twinning," corresponding to molecular orientations as follows:

Domain I:

$$(R_y, e_5, e_7) ,$$

Domain II:

$$\left(-\tfrac{1}{2}R_y + \frac{\sqrt{3}}{2}R_x,\ -\tfrac{1}{2}e_5 + \frac{\sqrt{3}}{2}e_4,\ -\tfrac{1}{2}e_7 + \frac{\sqrt{3}}{2}e_6\right) ,$$

and

Domain III:

$$\left(-\tfrac{1}{2}R_y - \frac{\sqrt{3}}{2}R_x,\ -\tfrac{1}{2}e_5 - \frac{\sqrt{3}}{2}e_4,\ -\tfrac{1}{2}e_7 - \frac{\sqrt{3}}{2}e_6\right) .$$

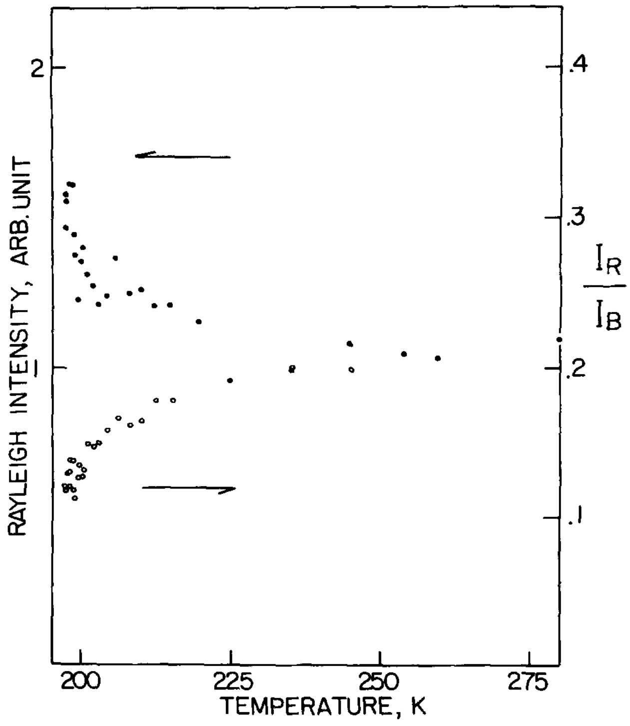

FIG. 5. Rayleigh intensity vs temperature (solid circles) and the intensity ratio I_R/I_B (open circles) vs temperature for *sym*-triazine.

One can concentrate on domain I without loss of generality and the free energy then becomes

$$F = \tfrac{1}{2}a_0(T - T_0)R_y^2 + \tfrac{1}{3}bR_y^3 + \tfrac{1}{2}cR_y^4 + \tfrac{1}{2}c_{44}^0 e_5^2 + \tfrac{1}{2}c_{66}^0 e_7^2$$

$$+ c_{14}^0 e_5 e_7 - A e_5 R_y + B e_7 R_y + \tfrac{1}{2}C e_5 R_y^2 - \tfrac{1}{2}D e_7 R_y^2 + \cdots . \qquad (2)$$

in which $c_{66}^0 = \tfrac{1}{2}(c_{11}^0 - c_{12}^0)$.

Forces conjugate to R_y, e_5, and e_7 can be defined in the the usual way as

$$\xi = (\partial F/\partial R_y) = a_0(T - T_0)R_y - Ae_5 + Be_7 + Ce_5 R_y - De_7 R_y ,$$

$$X_5 = (\partial F/\partial e_5) = c_{44}^0 e_5 + c_{14}^0 e_7 - AR_y + \tfrac{1}{2}CR_y^2 ,$$

$$X_7 = (\partial F/\partial e_7) = c_{66}^0 e_7 + c_{14}^0 e_5 + BR_y - \tfrac{1}{2}DR_y^2 . \qquad (3)$$

For an unclamped crystal $(\xi = 0)$, the effective elastic constants in the high temperature phase $(R_y = 0)$ can be calculated from their definitions

$$c_{44} = \left(\frac{\partial X_5}{\partial e_5}\right) = c_{44}^0\, \frac{T - T_1}{T - T_0} , \quad T_1 = T_0 + \frac{A^2}{a_0 c_{44}^0} , \qquad (4)$$

and

$$c_{66} = \left(\frac{\partial X_7}{\partial e_7}\right) = c_{66}^0\, \frac{T - T_2}{T - T_0} , \quad T_2 = T_0 + \frac{B^2}{a_0 c_{66}^0} .$$

Both constants have a common expression

$$c_{\text{eff}} = c_0\, \frac{T - T_3}{T - T_0} , \quad T_3 > T_0 . \qquad (5)$$

Within the framework of the Landau mean field theory, fluctuation effetts expressed by the cubic terms like $e_5 R_y^2$ and $e_7 R_y^2$ in Eq. (2) are not taken into consideration. Such fluctuations can also contribute to the elastic anomalies as reported by Yoshihara *et al.*[9] for the ferroelectric-ferroelastic phase transition in benzil. Equation (4), however, fully accounts for the experimental results for the *sym*-triazine soft mode assuming that the base transition temperature T_0 is given by the theoretical estimate -759 K and $T_1 = 180$ K and $T_2 = 17$ K.

As the scattering plane for these results lies almost in the crystal *ab* plane, we can assume that the phonons observed propagate in the *ab* plane. Effects of the elastic constants related to the *c* axis can be treated, therefore, by perturbation theory, as the observed temperature dependences are strong. Then the equations of motion for the acoustic phonons can be written in compact form as

$$\rho\omega^2(\mathbf{v}) = \mathbf{q}^2 \begin{pmatrix} c_{11}\cos^2\theta + c_{66}\sin^2\theta & \frac{1}{4}(c_{11}+c_{12})\sin 2\theta & c_{14}\cos 2\theta \\ \frac{1}{4}(c_{11}+c_{12})\sin 2\theta & c_{11}\sin^2\theta + c_{66}\cos^2\theta & -c_{14}\sin 2\theta \\ c_{14}\cos 2\theta & -c_{14}\sin 2\theta & c_{44} \end{pmatrix} (\mathbf{v}) , \qquad (6)$$

in which (v) represents the displacement vector of the acoustic phonons. In the dynamical matrix, elastic constant c_{14} gives the coupling between in-plane and out-of-plane motions and usually has a smaller value than the other components.[9] One can thereby neglect c_{14} in Eq. (6) as a first approximation. The eigenvalues can then be readily obtained

$$\rho\omega_1^2 = c_{44}\mathbf{q}^2$$

and

$$\rho\omega_\pm^2 = \frac{\mathbf{q}^2}{2}\{(c_{11}+c_{66}) \pm [(c_{11}+c_{66})^2 - (c_{11}^2 + c_{66}^2)\sin^2 2\theta - 4c_{11}c_{66}(\cos^4\theta + \sin^4\theta) + \tfrac{1}{4}(c_{11}+c_{12})^2 \sin^2 2\theta]^{1/2}\}. \qquad (7)$$

Rearranging terms inside the square root, one obtains

$$\rho\omega_+^2 = c_{11}q^2 \text{ and } \rho\omega_-^2 = c_{66}q^2 .$$

Under these assumptions, the phonon frequencies are independent of propagation direction in the *ab* plane. For the sample rotated 90° from its initial orientation in the *ab* plane, observed phonon frequencies are very close to the values obtained in the initial orientation (Fig. 3). This result seems to support these approximations (i.e., c_{14} is small).

An inequality $e_5 \gg e_1 - e_2 = e_7$ holds for the spontaneous values as shown in Fig. 3 of Ref. 8. Equation (3) gives relations between spontaneous values of the strains and order parameters

$$(e_5)_s \sim \frac{A}{c_{44}^0}\langle R_y\rangle \text{ and } (e_7)_s \sim \frac{B}{c_{66}^0}\langle R_y\rangle .$$

Thus, the rotation-translation coupling constant A is much larger than the constant B and the c_{44} softening is more pronounced than the c_{66} softening, as shown in Fig. 4.

Assigning the ω_1 mode to the T_1 mode, the ω_- mode to the T_2 mode, and the ω_+ mode to the L mode, the Landau mean field theory gives a consistent interpretation of the present Brillouin scattering results.

B. Dynamics and fluctuations

Molecular rotations play an important role in phase transitions in molecular solids through rotation-translation coupling. Traditionally, large amplitude rotation has been treated by introducing "pseudospin" as a stochastic variable.[11] This approach is quite successful in describing the statics and dynamics of phase transitions in the ammonium halides,[13] for example. On the other hand, a librational phonon or libron model gives a good description of small amplitude rotation. Unfortunately, most real (molecular) crystals cannot be definitely classified as one or the other of these extreme cases.

Michel and Naudts[12] have developed a different approach to this problem introducing "symmetry adopted functions" as rotational variables; they have successfully explained the ferroelastic phase transition in KCN which is triggered by rotational motion of the CN⁻ ion.[14]

Recently Raich *et al.*[10] extended the mean field theory of *sym*-triazine to discuss dynamic properties near the phase transitions using an equations of motion approach. The Hamiltonian consists of three parts

$$\mathcal{H} = \mathcal{H}^T + \mathcal{H}^R + \mathcal{H}^{R-T} , \qquad (8)$$

in which $\mathcal{H}^T$ is the translational Hamiltonian expressed in acoustic phonon modes,

$$\mathcal{H}^T = \frac{1}{2}\sum_{\mathbf{k}}\sum_{j=1}^{3} P(\mathbf{k}j)P(-\mathbf{k}j) + \omega_j^2(\mathbf{k})Q(\mathbf{k}j)Q(-\mathbf{k}j) , \qquad (9)$$

and $\mathcal{H}^R$ is the rotational part including rotational kinetic energy

$$\mathcal{H}^R = \frac{h^2}{2I}\sum_{\mathbf{k}}\sum_{\alpha=x,y} L_\alpha(\mathbf{k})L_\alpha(-\mathbf{k}) + V . \qquad (10)$$

In Eq. (10) $I = I_x = I_y$ is the moment of inertia of the *sym*-triazine molecules in the molecular plane and V is the rotational potential. Only crystal field potential terms which have trigonal symmetry will be considered in this case. They are expressed by tesseral functions

$$V = \sqrt{N}(a_{20}\mathcal{S}_{20} + a_{40}\mathcal{S}_{40} + a_{43}\mathcal{S}_{4-3}) . \qquad (11)$$

The last term in Eq. (8) contains rotation-translation coupling and has the general form

$$\mathcal{H}^{RT} = \sum_{\mathbf{k}}\sum_{j=1}^{3}\sum_{L,M} g_{jM}^L(\mathbf{k})Q(\mathbf{k}j)\mathcal{S}_{LM}(-\mathbf{k}) . \qquad (12)$$

Details of the allowed coupling constants needed to calculate phonon-phonon correlation functions which can be directly observed by neutron and light scattering experiments are found in Ref. 10. As a consequence of the Hamiltonian (Eq. (8)) and commutation relations, the equations of motion lead to a chain of equations for the Green's functions.[17] Truncating this series in the manner of mean field theory, one arrives at a system of equations which can be written in a matrix form as,

$$\mathbf{DG} = \mathbf{\Delta} , \qquad (13)$$

in which **D** is the dynamical matrix for the Green's functions, **G** is the Green's function matrix, and **Δ** is a diagonal matrix whose elements are ±1 depending on the components.

In the high-temperature approximation $kT \gg \hbar\omega$, correlation functions are given by a general formula

$$\phi_{kl}(\omega) = -\frac{2kT}{\hbar\omega}\,\Delta_{ll}\,\mathrm{Im}[(D^{-1})_{kl}]\ . \qquad (14)$$

These correlation functions are just a generalization of those obtained by Yamada *et al.*[11] for ammonium halides and Michel and Naudts[12] for alkali cyanides for propagating rotational modes. Choosing suitable values for parameters in Eq. (14), the results of these authors can be reproduced.

For small amplitude librations, observed by Raman scattering around 60 cm^{-1} in *sym*-triazine, the tesseral functions for $L=2$ can be expanded in rotational coordinates R_x and R_y as follows[18]:

$$S_{20} \sim 1 - \tfrac{3}{2}(R_x^2 + R_y^2),\quad A_g\ ,$$

$$\left.\begin{array}{l} S_{21} \sim R_y\ , \\ S_{2-1} \sim -R_x\ , \end{array}\right\}\ E_g\ ,$$

and

$$\left.\begin{array}{l} S_{22} \sim R_x^2 - R_y^2\ , \\ S_{2-2} \sim R_x R_y \end{array}\right\}\ E_g\ .$$

With this substitution the Hamiltonian then reduces to a "rotation–translation–spin" coupled system. "Spin" variables are related to fluctuations in excited phonon numbers in the doubly degenerate rotational state and are of quadratic or higher form in R_x and R_y. Using this approach Raich *et al.*[10] have been able to obtain a good numerical fit to the observed neutron scattering response function.

For the "spin–phonon" system one can identify two limits:

(1) Fast relaxation–relaxation times for the spin variables are much shorter than the phonon oscillation period. In this instance, the phonon frequency softens but no central peak enhancement obtains. KCN is close to this limit.[14]

(2) Slow relaxation–spin relaxation time is much longer than the phonon oscillation period. Critical slowing down of the relaxation time obtains and a well defined central peak grows without a soft phonon response. This is the case for NH$_4$Br.[13]

In the present experiment, a well defined (under damped) soft mode phonon is observed but no central peak response appears (Figs. 4 and 5). Therefore, we can interpret the *sym*-triazine transition as a fast relaxation case in the terminology of spin–phonon systems.

Nonetheless, an increasing of the Rayleigh intensity is observed near the transition temperature. There are two possible explanations for this result:

(1) The transition is actually an example of an intermediate case but close to the fast relaxation extreme, or (2) critical fluctuations occur in the high temperature phase. These two possibilities are now explored.

The phonon frequencies obtained in the neutron scattering study are much higher than those found in the Brillouin scattering ($\omega_N \gg \omega_B$), due to large differences in observed phonon wave vectors. The condition for fast relaxation is given by $\omega\tau \ll 1$, in which τ is the relaxation time. Even if one assumes an intermediate case response for the neutron experiment, a fast relaxation response is obtained for the Brillouin experiment; i.e.,

$$\omega_B\tau \ll \omega_N\tau \sim 1\ . \qquad (15)$$

This result tends to eliminate the first possibility above for the Brillouin scattering experiment. Therefore, the phase transition of *sym*-triazine falls in the fast relaxation limit.

Thereby, within the framework of a dynamical mean field treatment, no central peak can be expected. However, if the mean field results are taken as a base only, and if deviations from the mean field theory are supposed, the Rayleigh intensity results may be rationalized.

The present results on the elastic constants, however, show no clear deviations from the mean field results even for temperatures quite near the phase transition temperature for which the Rayleigh intensity is found to increase. If critical fluctuations exist around the transition temperature which contribute to the Rayleigh intensity anomaly but not the elastic constant anomalies, their frequencies must be lower than the soft-phonon frequency by analogy with the slow-relaxation limit. Such fluctuations could arise through higher-order (anharmonic) couplings of the independent $c_{44}(e_4, e_5)$ and $c_{66}(e_6, e_7)$ instabilities. Based on correlation data, these fluctuation frequencies must be outside the range 1 to 10^{-6} s.

V. CONCLUSIONS

We have investigated the ferroelastic phase transition in *sym*-triazine around 197 K by Brillouin scattering and correlation spectroscopy. Our observations are summarized as follows:

(1) A soft mode whose squared frequency satisfies a mean field result given by

$$\omega_S^2 = (\omega_S^0)^2\,\frac{T-180}{T+759}$$

was characterized. This c_{44} instability is considered as the physical origin of the phase transition.

(2) No well defined central peak could be observed in the Brillouin spectra, but a 50% increase of the Rayleigh intensity was observed near the transition temperature in the high temperature phase.

(3) A second independent, temperature dependent TA phonon was observed which also satisfies mean field behavior

$$(\omega_S')^2 = (\omega_S'^0)^2\,\frac{T-17}{T+759}\ .$$

This mode is interpreted as a result of a c_{66} instability not directly "related to" or "driven by" the c_{44} "main" instability.

(4) The LA phonon does not show any anomaly even near the transition temperature.

(5) Correlations in the Rayleigh scattering were not observed at any temperature ($T \geq T_t$) between roughly 10^{-6} and 1 s.

These results are interpreted by a Landau mean field theory and a dynamical theory. Both approaches give a consistent explanation for the static and dynamic Brillouin and neutron scattering data. Based on the dynamical theory, the phase transition in *sym*-triazine can be regarded as an example of the fast-relaxation case which is characterized by a soft-mode phonon response without a central peak.

Finally, the possibility of critical fluctuations was examined using the Rayleigh intensity and correlation results. These data suggest that the only possibility for fluctuation effects near the transition temperature is for fluctuation frequencies smaller than 1 Hz or between 10 MHz and 1 GHz.

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[18] It has been pointed out to us by T. Luty (private communication) that, based on lattice dynamical calculations, the optical modes containing the molecular rotations R_x and R_y are mixed with translations. In this sense the treatment of Refs. 8 and 10 become approximate.