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Citation: The Journal of Chemical Physics **73**, 1955 (1980); doi: 10.1063/1.440284
View online: http://dx.doi.org/10.1063/1.440284
View Table of Contents: http://aip.scitation.org/toc/jcp/73/4
Published by the American Institute of Physics

On the phase transition in *sym*-triazine-mean field theory

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(Received 24 March 1980; accepted 29 April 1980)

A Landau mean field description of the nearly second order phase transition in *sym*-triazine crystals at ~ 200 K is presented. A model Hamiltonian is generated which consists of the appropriate symmetry elastic constant terms, molecular rotational energy, and rotation–translation coupling terms (to second order in both strains and rotations). Due to the symmetry of the crystal in the high ($R\bar{3}c$) and low ($C2/c$) temperature phases, third order terms in the rotational order parameter are nonvanishing; the transition is thereby a first order one (although only weakly so). This Hamiltonian is then converted to a free energy by addition of an entropy term calculated for an orientation distribution (about the z axis) based on pocket state functions. The Landau mean field model is developed by choosing a set of order parameters R_y (molecular rotation about the y axis) and strains e_5 and (e_1-e_2). The free energy expression is used to calculate relations between order parameters by setting $\partial F/\partial R_y = \partial F/e_5 = \partial F/\partial e_7 = 0$. Coupling terms including bilinear products of e_ρ's and R_y are employed in this development. Renormalized temperature dependent elastic constants are derived. $e_5(T)$ is solved for and found to be in good agreement with observed temperature dependences. Librational frequencies are determined from $(\partial^2 H/\partial R_i R_j)_{e_p} = I\omega_i^2\delta_{ij}$. It is found that in the low temperature phase $\Delta\omega = |\omega_y - \omega_x| \propto e_5$ in lowest order. Observed power laws for frequencies, splittings and strains with respect to $\epsilon \equiv (T - T_c/T)$ are discussed in light of these new results. The role of third order terms in (R_x, R_y) is considered and found to be an important factor in apparent deviation from mean field exponents.

I. INTRODUCTION

Progress in our understanding of phase transitions and critical phenomena has been dramatic in recent years. In particular, a recognition of the universal nature of phase transition and critical dynamics as well as a reformulation of these concepts in terms of an abstract theoretical framework[1] have been especially significant in the continued vitality of this field. These developments have, of course, sparked experimental activity as well. Although phase transitions in simple molecular solids such as H_2, N_2, and CH_4 have been studied extensively, experimental and theoretical interest in solid–solid transitions in more complex molecular crystals is only relatively recent.[2]

As a class, molecular solids should occupy a rather central position in both theoretical and experimental investigations of solid–solid phase transitions for three reasons: (1) they have short range interactions; (2) they have well-characterized structures and constituents; and (3) they are easy to handle, purify, and grow. Of particular significance for experimental considerations is the importance of short range interactions for the width of the critical region.[1,2a–b] A dimensional analysis argument can readily be made showing that the temperature or pressure width of the critical region is inversely proportional to the characteristic range of the interactions in the crystal. Therefore, it may well be that critical phenomena and critical behavior are much more accessible in molecular solids than in ionic ones. Moreover, at least several molecular solid phase transitions do not appear to be explicable in terms of mean field (infinite range interaction)–soft mode theory.[1a,2]

This paper presents a theoretical investigation of the phase transition in a well-studied molecular crystal, *sym*-triazine ($C_3N_3H_3$). The phase transition in triazine was first located by x-ray structure investigations,[3] and then characterized by subsequent optical spectroscopy at zero and high electric and magnetic fields,[4] Raman scattering,[5–7] NQR measurements,[8] Rayleigh–Brillouin acattering,[9] heat capacity measurements,[10,11] and x-ray[12] and neutron scattering studies.[13] In addition, an attempt has been made to treat the phase transition theoretically and to reconcile some of these various data.[14] This latter theoretical effort is quite useful in identifying an order parameter for the transition but still leaves a number of questions open concerning the detailed mechanism and overall dynamics for the transition. The details of the coupling between the elastic modes and molecular rotations have been omitted in previous studies, and thus a full elucidation of the transition based on a classical Landau-type treatment has not been presented.

The major conclusions that can be drawn from these earlier studies of the triazine phase transition are as follows:

1. the transition is from a high temperature (atmospheric pressure) trigonal phase with space group D_{3h}^6 ($R\bar{3}c$) to a low temperature (high pressure) monoclinic phase with space group C_{2h}^6 ($C2/c$);
2. the transition is first order, although only weakly so;
3. the shear strain component $e_{zx}(e_5)$ is an order parameter for the structural deformation;
4. molecular rotation out of the (x, y) plane, (R_x, R_y), appears to be a reasonable orientational order parameter;

[a)] Supported by NSF Grant DMR16-187380.

[b)] Supported in part by a grant from AFOSR.

5. anomalous behavior has been found for the transverse acoustic shear modes governed by the elastic constant c_{44};

6. anisotropic multipolar intermolecular interactions seem to be necessary to stabilize the low temperature structure; and

7. except in the immediate neighborhood of the transition, the thermodynamics seem adequately described by a Landau mean field description.

The approach taken in this work to a theoretical description of the triazine transition is to construct a model system which, within mean field constraints, can be solved in some detail. Results and conclusions based on this model may then be compared with experimental data in order to determine which aspects of the triazine behavior can be analyzed in terms of this classical limit. A Hamiltonian is introduced which includes rotational and elastic energies as well as a coupling between elastic strain components and rotational motion of the molecules out of the trigonal basal plane. Using this Hamiltonian, an expansion of the free energy of the triazine crystal is developed in terms of orientational and strain order parameters. Within a Landau mean field approach the temperature dependences of these order parameters are calculated and compared with x-ray diffraction results. Anomalous behavior of the elastic constants c_{44}, $\frac{1}{2}(c_{11}-c_{12})$, and c_{14} is predicted. Splittings of various spectroscopic features due to the change in symmetry at the structural transformation are discussed. The Landau-type mean field approach is applicable in situations for which third order terms in the free energy expansion are small so that first order character can be observed only close to the transition and hence the transition can be considered as nearly second order. Because of the similarities in the crystal structures, our overall approach is similar to that taken for the ionic solid, sodium azide.[15] In the final section, discussion is devoted to possible future elaborations of this approach and to the need for additional lattice dynamical and experimental studies.

The aim of the present investigation is to explore the nature of the structural transformation in triazine and to define soft-mode behavior in this example of a ferrodistortive transition in a molecular crystal. Our ultimate goal is to elucidate the physical mechanism of the structural phase transition.

II. STRUCTURAL TRANSFORMATION

X-ray[2,12] and neutron diffraction[13] investigations report a structural phase transition in triazine at $T_c = 199$ K and $p = 1$ atm. The high temperature (low pressure) structure is given as trigonal or rhombohedral, D_{3d}^6 ($R\bar{3}c$), with two molecules per primitive unit cell at sites of average $D_3(32)$ symmetry. The low temperature (high pressure) structure is monoclinic, $C_{2h}^6(C2/c)$, with two molecules per primitive unit cell at sites of $C_2(2)$ symmetry. The transition is said to be "almost second order" with a small latent heat.[10] The transition temperature is found to increase linearly with pressure accordint to $T_c(p) = 198.9 + 18.2p$, where T is in K and p is in kbar.[8] The high temperature structure of triazine is shown in Fig. 1. The crystalline x axis is choen to run between N and C atoms of the central molecule of the figure, and the z axis is perpendicular to the molecular plane. For this choice of coordinate axes the x axis is oriented 30° from the hexagonal a_h axis, which runs through an N or C atom.[3,13,14] This choice of axes is retained for the monoclinic phase.

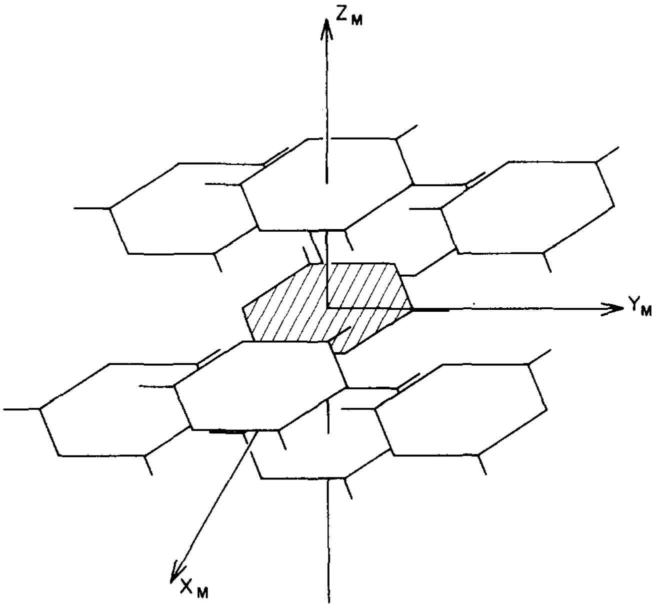

FIG. 1. The crystal structure of triazine for the trigonal phase at room temperature and atmospheric pressure. Only the nearest and next-nearest neighbors of a particular molecule at the center (shaded darker) are shown. The monoclinic axes x_M, y_M, and z_M are indicated. The x_{11} axis is chosen to bisect a C–N bond of the central molecule. The y_M axis then coincides with a C–H bond.

The eigenvector generating the low temperature phase is that of an elastic shear (transverse acoustic) mode propagating in the monoclinic xy plane (hexagonal $a_h b_h$ basal plane) and polarized along the monoclinic z axis (hexagonal c_h axis).[13,14] The corresponding lattice strain is e_{zx} or e_5. The nature of this deformation is illustrated in Fig. 2. The deformation shown in Fig. 2 is drawn in the monoclinic $(xz)_M$ plane. This corresponds to one of three possible triple-twinned domain structures; the other two are related to the one of Fig. 2 by rotation of 120° about the z axis.

The strain e_5 is related to the change in $\cot\beta_M$. Here a_M, b_M, c_M, and β_M are monoclinic cell parameters, as shown in Fig. 2(b), and defined by Smith and Rae.[12] The change in the monoclinic angle $\alpha_M = \beta_M - 90°$ was identified as the order parameter for the transition by Rae.[14]

Figure 3 shows the temperature dependence of $|\Delta(\tan\alpha_M)|$ for the data of Smith and Rae.[12] The temperature dependence of the shear angle α_M was previously thought to be fairly well described by a power law of the form $(T_c - T)^\beta$, with an exponent $\beta \cong \frac{1}{2}$. This conclusion is supported by NQR studies of the transition as a function of pressure. This value of the exponent β suggests a Landau or mean field description for the phase transi-

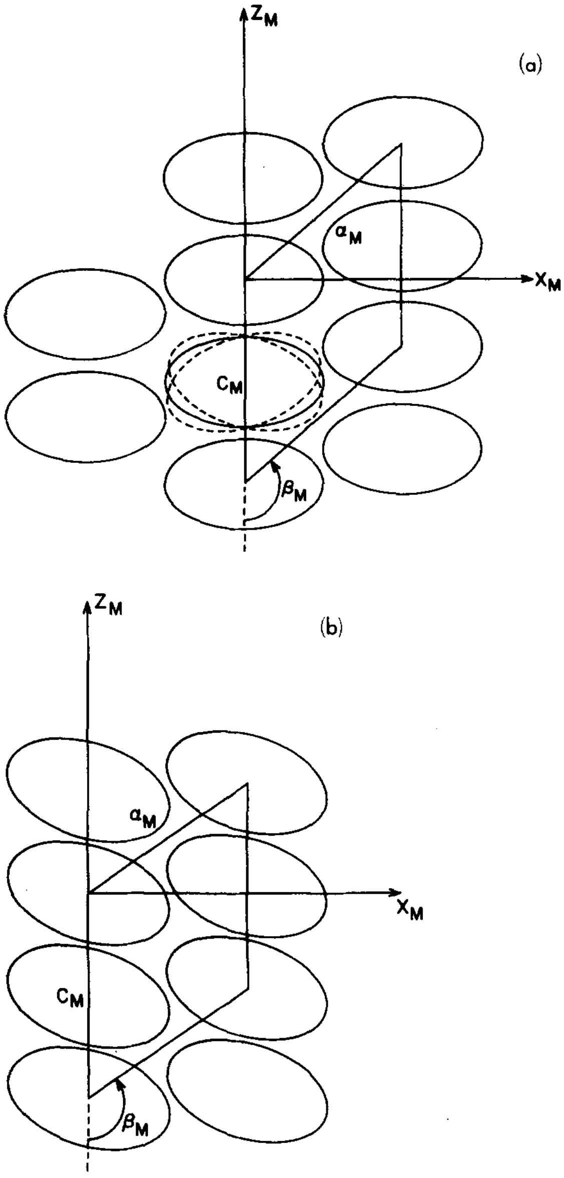

FIG. 2. A cut through the $(xz)_M$ plane of Fig. 1. The triazine molecules are represented by the ellipsoids, which roughly correspond to their shape. Part (a) shows the molecular orientations in the high temperature phase. The dashed curves indicate the orientations of the central molecule with its axis tilted by ± 17.5°. Part (b) shows the molecular orientations in the low temperature phase. Little orientational freedom remains.

tion. Such mean field behavior is also substantiated by the absence of a high temperature tail for the heat capacity, which indicates no order parameter correlations above T_c.[10,11] For comparison, a $(T_c-T)^{1/2}$ behavior for the strain is also indicated on Fig. 3. Deviation of the data from a simple mean field power law is noticeable.

One reason for the poor fit of a $\beta=1/2$ exponent is that the data of Smith and Rae indicate a small discontinuity in the strain order parameter at the transition temperature. Thus, as found also from heat capacity measurements ($\Delta H_{\mathrm{trans}}\cong 75$ J mol^{-1}),[10] there is a small first-order character to the transition. This is to be expected from an application of the Lifshitz criterion to a $D_{3d}\rightarrow C_{2h}$ transition. This transformation involves a reduction by a factor of 3 in the number of point group symmetry elements. Hence, according to group-theoretical considerations, this transition will have nonzero third order terms in the expansion of the free energy and, consequently, will not be strictly of second order.[15]

In Fig. 3 we have also included the results of Smith and Rae[12] for the strain $e_{xx}-e_{yy}=e_1-e_2\equiv e_7$. Here $e_1\sim\Delta a_{Mx}/a_{Mx}$ and $e_2\sim\Delta b_M/b_M$, where $a_{Mx}=a_M\sin\beta_M$. Plotted in Fig. 3 is $\Delta a_{Mx}/a_{Mx}$. These results indicate that the strain e_7 is very small, if it is at all present. Therefore, one concludes that the trigonal to monoclinic deformation can be described in terms of the strain order parameter e_5.

Stability criteria for crystals of trigonal classes $\bar{3}m(D_{3d})$ have been outlined by Cowley.[16] The strain e_5 belongs to the irreducible representation E_g, with strain basis functions $[e_5, e_6]$ and $[e_1-e_2\equiv e_7, e_4]$. Cowley states that for this representation there is in general no acoustic wave whose velocity is zero when the corresponding elastic constant stability condition

$$(c_{11}-c_{12})c_{44}-2c_{14}^2>0 \qquad (1)$$

is violated (equal to zero). The elastic constant matrix $c_{\rho\sigma}$ is tabulated in Appendix A for the trigonal classes.

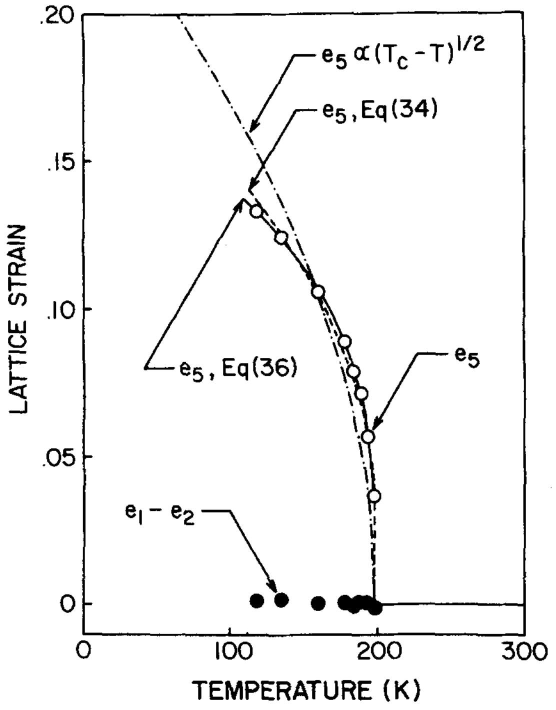

FIG. 3. The lattice strain as a function of temperature. The solid dots represent the data of Ref. 12 for $\Delta a_{Mx}/a_{Mx}$, which measures the strain (e_1-e_2). The empty circles indicate the data of Ref. 12 for $|\Delta(\cot\beta_M)|$, where β_M is the monoclinic cell angle. This quantity measures the strain component e_5. For comparison, the dashed line indicates a $(T_c-T)^\beta$ dependence. Here $\beta=\frac{1}{2}$ according to Landau's theory of second order phase transitions. Also show is a fit to the data using Eqs. (34) and (36) for $e_5(T)$.

However, there are special instances for which an acoustic mode velocity will vanish. The diagonalization of the dynamical matrix

$$M_{\alpha\beta}(\mathbf{q}) = \sum_{\gamma\lambda} c_{\alpha\gamma\beta\lambda} q_\gamma q_\lambda \tag{2}$$

is outlined in Appendix B. For the $[00\zeta]$ direction the transverse acoustic mode velocity $V_{\mathrm{TA}} \sim \sqrt{c_{44}}$. It also follows from Appendix B that one of the the transverse sound velocities in the $[\xi 00]$ direction will vanish if stability condition (1) is equal to zero. In the $[0\eta 0]$ direction will vanish is stability condition (1) is equal to zero. In the $[0\eta 0]$ direction, one of the transverse sound velocities is proportional to $\sqrt{\frac{1}{2}(c_{11} - c_{12})}$.

The softening of the $[00\zeta]_{\mathrm{TA}}$ and the $[\xi 00]_{\mathrm{TA}}$ acoustic modes has recently been observed by inelastic neutron scattering.[13] This softening was found to extend considerably in the Brillouin zone and was attributed to an instability of the c_{44} elastic constant. In these measurements phonon modes remain well defined and underdamped down to temperatures close to the transition temperature, T_c. Below T_c, the modes stiffen again quickly. It has been proposed[13] that the phase transition in triazine results from an elastic instability and is therefore accompanied by a softening of a $\mathbf{q} = 0$ acoustic mode.[16,17]

A group theoretical analysis of the phase transition in triazine can be carried out in the same manner as for sodium azide,[15] since the space groups of the high and low temperature phases are similar. As for sodium azide the transformation proceeds as $D_{3d} \to C_{2h}$. The representation E_g of D_{3d} contains the totally symmetric representation A_g of C_{2h}. Hence order parameters for the system can have E_g symmetry (in the high temperature phase). Relevant strain order parameters are $(e_1 = -e_2, e_4)$ and (e_5, e_6), with e_5 being dominant.

The lattice deformation, characterized by the above strains with E_g symmetry, is accompanied by a tilt of the axis of the triazine molecules. This tilting occurs about the monoclinic y axis for the domain of Fig. 2. In general, tilting of the molecules is described by (R_x, R_y), that is, rotations about the monoclinic x_M and y_M axes. For $D_{3d}(R_x, R_y)$ also transform as E_g.

Reorientation of the molecular planes is clearly coupled to (expressible in terms of) lattice strains. Because both are of the same symmetry type, bilinear and higher order coupling terms between (R_x, R_y) and the e's exist. This coupling can be expected to lead to an indirect triazine–triazine interaction which results in a reorientation of molecules in the low temperature phase. This type of phase transition is classified as ferroelastic.[16,17] Examples of ferroelastic phase behavior are found in the alkali cyanides[18–23] and azides[15]; a more extensive list can be found in Ref. 17. The extent of the orientational disorder in the high temperature phase varies considerably for different materials and structures.[15]

III. ORIENTATIONAL DISTRIBUTION FUNCTION AND ENTROPY

Long-range orientational order of triazine molecules at a temperature T can be described by a single particle orientational distribution function $P(\Omega)$. The probability that the molecule has its axis directed within the solid angle $d\hat{\Omega} = \sin\theta\, d\theta\, d\phi$, about the direction $\hat{\Omega} = (\theta, \phi)$, is given by $P(\hat{\Omega}) d\hat{\Omega}$. The orientational distribution function can be expanded in terms of symmetry-adapted spherical harmonics or rotation matrices, as will be discussed in Sec. IV.

Molecular orientations in both trigonal and monoclinic phases of triazine are well defined relative to certain equilibrium orientations. Hence an expansion of $P(\hat{\Omega})$ in terms of spherical harmonics would be cumbersome, and it might actually be much more efficient to use a pocket state formalism.[15,24] In the case of extremely localized orientational pockets, the pocket state distributions can be approximated by delta functions. Because of the threefold symmetry of the triazine crystal, one writes

$$P(\hat{\Omega}) = P_1 \delta(\hat{\Omega} - \hat{\Omega}_1) + P_2 \delta(\hat{\Omega} - \hat{\Omega}_2) + P_3 \delta(\hat{\Omega} - \hat{\Omega}_3) , \tag{3}$$

in which

$$\hat{\Omega}_i = (\theta_i, \phi_i) , \quad i = 1, 2, 3 ,$$

are the three possible orientations of the molecules about the threefold axis of the crystal. It should be pointed out that the sum of delta functions (3) is a very rough approximation to the actual orientational distribution function for triazine. This distribution function probably resembles that of sodium azide,[15] which points along the threefold axis, but has a slightly triangular shape. Some degree of orientational disorder is, however, expected in the high temperature phase of triazine as well. For the choice of coordinates gigen in Fig. 2, $\phi_1 = 0$, $\phi_2 = 2\pi/3$, and $\phi_3 = 4\pi/3$.

If one defines

$$x_i = \cos\phi_i , \quad y_i = \sin\phi_i ,$$

then

$$x_1 = 1 , \quad y_1 = 0 .$$

$$x_2 = -\tfrac{1}{2} , \quad y_2 = \sqrt{3}/2 ,$$

$$x_3 = -\tfrac{1}{2} , \quad y_3 = -\sqrt{3}/2 ,$$

Averages are found according to

$$\langle x \rangle = \int P(\hat{\Omega})\, x\, d\hat{\Omega} = \sum_{i=1}^{3} P_i x_i . \tag{4}$$

Equation (4) then yields the relations

$$P_1 = \tfrac{1}{3} + \tfrac{2}{3}\langle x \rangle ,$$

$$P_2 = \tfrac{1}{3} - \tfrac{1}{3}\langle x \rangle + \langle y \rangle/\sqrt{3} ,$$

$$P_3 = \tfrac{1}{3} - \tfrac{1}{3}\langle x \rangle - \langle y \rangle/\sqrt{3} .$$

For small tilt angles θ_i one may identify rotations about the x- and y axes as

$$R_x = -\langle y \rangle \text{ and } R_y = \langle x \rangle ,$$

so that

$$\begin{aligned} P_1 &= \tfrac{1}{3} + 2R_y/3 , \\ P_2 &= \tfrac{1}{3} - R_y/3 - R_x/\sqrt{3} , \\ P_3 &= \tfrac{1}{3} - R_y/3 + R_x/\sqrt{3} . \end{aligned} \tag{5}$$

The orientational entropy of the crystal is

$$S = -Nk_B \int P(\hat{\Omega}) \ln P(\hat{\Omega}) d\hat{\Omega} = -Nk_B \sum_{i=1}^{3} P_i \ln P_i \ , \qquad (6)$$

where N is the number of molecules and k_B is Boltzmann's constant. Using Expressions (5) for the orientational distribution (3) and expanding for small rotations (R_x, R_y), the orientational entropy part of the free energy per molecule is

$$-\frac{1}{N} TS = -\text{const}\,T + k_B T(R_x^2 + R_y^2) - k_B T(R_y^3 - 3R_x^2 R_y) + \tfrac{3}{2} k_B T(R_x^2 + R_y^2)^2 + \cdots \ . \qquad (7)$$

This formulation of the change in ordering of molecular orientations implies a certain degree of disorder of these orientations in the high temperature phase, similar to that observed for sodium azide,[15] and pointed out previously for the case at hand.[2,4]

IV. FERROELASTIC INTERACTIONS

A. Elastic energy density

The elastic energy density is

$$\frac{U_E}{V} = \frac{1}{2} \sum_{\alpha\beta\gamma\lambda} c_{\alpha\beta\gamma\lambda} e_{\alpha\beta} e_{\gamma\lambda} \ . \qquad (8)$$

The elastic constant matrix for the present problem is tabulated in Appendix A. The result for D_{3d} $(\bar{3}m)$ is, in Voigt notation,

$$\mathcal{H}_E = \frac{U_E}{V} = \frac{1}{2} \frac{c_{11}^0 + c_{12}^0}{2} (e_1 + e_2)^2 + \tfrac{1}{2} c_{33}^0 e_3^2 + c_{13}^0 (e_1 + e_2) e_3 + \tfrac{1}{2} c_{44}^0 (e_4^2 + e_5^2) + \frac{1}{2} \frac{c_{11}^0 - c_{12}^0}{2} (e_6^2 + e_7^2) + c_{14}^0 (e_5 e_7 - e_4 e_6) \ . \qquad (9)$$

Here, as above, we have defined $e_7 \equiv e_1 - e_2$. The superscripts 0 on the elastic constants indicate that these c^0's are relatively temperature independent. Here V is the volume of the crystal.

B. Orienting potential

The general form of the rotational energy, as an expansion in R_x and R_y, can be deduced from the symmetry of the problem. For D_{3d} symmetry the expansion has the form

$$\mathcal{H}_R = \tfrac{1}{2} a(R_x^2 + R_y^2) + \tfrac{1}{3} b(R_y^3 - 3R_x^2 R_y) + \tfrac{1}{4} c(R_x^2 + R_y^2)^2 + \cdots \ , \qquad (10)$$

where the averages $\langle \cdots \rangle$ have been left off. Since $\mathcal{H}_R$ contains both a crystal field and a mean field due to molecule–molecule anisotropic interactions, the coefficients a, b, c, ... are in general temperature dependent. Crystal field terms are, however, expected to dominate for triazine, as will be indicated below. Note that Eq. (10) has the same form as the free energy introduced by Rae of the shear angles (θ, ϕ).[14b]

By way of justification of this form as more than an abstract group theoretical construct, it is necessary to consider the nature of the intermolecular potential in a triazine crystal.

Ab initio calculations of Mulder, van Dijk, and Huiszon[25] indicate that long-range interactions between seven (*aza*) benzene molecules, including triazine, must be described in terms of anisotropic dispersion and induction interactions as well as multipole–multipole terms. They found that triazine is expected to behave much more like an octupole than a quadrupole, the latter moment being small. In the notation of Ref. 25 the quadrupole moment is $Q_{2,0} = 1.74$ a. u. and the octupole moment is $Q_{3,-3} = -88.1$ a. u. Since octupole–octupole interactions between neighboring triazine molecules seem to be the dominant multipolar coupling, one must specify the orientation of each molecule by three degrees of freedom. Therefore, one needs to expand the intermolecular interactions between two triazine molecules in terms of the rotation matrices $D_{mm'}^{l}(\alpha\beta\gamma)$.[26] Angular variables $(\alpha\beta\gamma)$ in the rotation matrices are the Eulerian angles representing the molecular orientations relative to the intermolecular axis connecting the two molecules.

The anisotropic dispersion, induction, and repulsion interactions between triazine molecules can be expanded in the same manner as the multipolar terms, but with a different R dependence. The determination of the relative importance of various contributions, i. e., dispersion, induction, multipolar, repulsive overlap, and perhaps hydrogen bonding[27,28] to an anisotropic triazine–triazine dimer interaction potential must await further elucidation of the details of the potential. However, one would expect that anisotropic repulsive interactions, as well as electrostatic hydrogen bond type C–H··· N interactions, will play an important role in the overall pair energy.

It is therefore reasonable to define an effective single particle potential for each triazine molecule, which represents the orienting field in which each molecule librates and reorients itself. This means the orientational field as the form

$$V^{\text{eff}} = \sum_{lmn} C_l^{mn} D_{mn}^{l}(\alpha\beta\gamma) \ . \qquad (11)$$

The coefficients C_l^{mn} depend on the average orientations of neighboring molecules and are in this manner dependent on temperature and order parameters.

For D_{3d} symmetry only the following terms will contribute to the sum (11):

$$Y_{20} (\equiv D_{00}^2) \ , \ Y_{40}, Y_{43}, Y_{4-3}, D_{m3}^{3*}, D_{m-3}^{3*} \ , \qquad (12)$$

It was noted previously that the rotations about the x and y axes, R_x and R_y, transformed according to the representation E_g and are thus proper orientational order parameters. It is therefore appropriate to express the orientational field (12) in terms of (R_x, R_y), for example,

$$\langle Y_{20} \rangle \sim 2R^2 - 3(R_x^2 + R_y^2) \ . \qquad (13)$$

The rotation matrices of Eq. (11) can be related to expressions involving R_x and R_y, like the above, but will in general contain the rotation about the threefold axis, R_z. For D_{3d}, R_z transforms according to A_{2g} and no bilinear coupling between R_z and the lattice strains with E_g symmetry can arise. Any coupling between the R_z libration and lattice deformations must occur in higher order and will be ignored in the present paper. This approach seems well justified in light of the structural findings discussed previously.

C. Rotation–translation coupling

Coupling of molecular rotations to lattice strains and orientational coordinates. A coefficient in the expansion of the rotation–translation coupling can exist only if the corresponding symmetric powers of (e_5, e_6), (e_7, e_4), and (R_x, R_y) belong to the same irreducible representation. Appropriate powers of strains and rotations and their products are found by the usual group theoretical techniques. For D_{3d} symmetry, allowed coupling terms are

$$\begin{aligned}\mathcal{H}_{RT} ={}& A(e_4R_x - e_5R_y) + B(e_6R_x + e_7R_y) + C\left(e_4R_xR_y - e_5\,\frac{R_x^2-R_y^2}{2}\right) + D\left(e_6R_xR_y + e_7\,\frac{R_x^2-R_y^2}{2}\right)\\ &+ E\left(e_4e_5R_x - \frac{e_4^2-e_5^2}{2}\,R_y\right) + G\left(e_6e_7R_x + \frac{e_6^2-e_7^2}{2}\,R_y\right)\\ &+ H\left(e_4e_5R_xR_y - \frac{e_4^2-e_5^2}{2}\,\frac{R_x^2-R_y^2}{2}\right) + I\left(e_6e_7R_xR_y + \frac{e_6^2-e_7^2}{2}\,\frac{R_x^2-R_y^2}{2}\right)\\ &+ J[(e_5e_6 - e_4e_7)R_x - (e_4e_6 + e_5e_7)R_y] + K[(-e_5e_6 - e_4e_7)R_xR_y + (e_4e_6 + e_5e_7)R_xR_y] + \cdots\,. \end{aligned} \tag{14}$$

$\mathcal{H}_{RT}$ may also be written in terms of the symmetry-adapted spherical harmonics. The Y_{lm}'s which occur in bilinear coupling terms, for example, are

$$Y_{21}^{s,c},\ Y_{22}^{s,c},\ Y_{41}^{s,c},\ Y_{42}^{s,c},\ Y_{44}^{s,c}\ ,$$

in which Y_{lm}^{c} and Y_{lm}^{s} are real linear combinations of Y_{lm} and Y_{l-m} with ϕ dependences $\cos(m\phi)$ and $\sin(m\phi)$, respectively.[15]

V. LANDAU MEAN FIELD MODEL

The free energy of a system of coupled triazine hindered rotators can be constructed from the total interaction energy

$$\mathcal{H} = \mathcal{H}_E + \mathcal{H}_R + \mathcal{H}_{RT}\ , \tag{15}$$

as given by Eqs. (9), (10), and (14), and an orientational entropy contribution of the type discussed in Sec. III. The potential energy surface specified by Eq. (15) in the space of the strain components $(e_4,\ e_5)$ and $(e_6,\ e_7)$ is the usual "Mexican hat" with three potential minima located away from the threefold axis. In the high temperature phase we expect some disorder in the molecular orientations, i.e., $R_x^2 + R_y^2 \neq 0$. The Mexican hat potential surface (15) then implies lattice deformations $[e_4^2 + e_5^2] \propto \alpha[R_x^2 + R_y^2]$ and $[e_6^2 + e_7^2] \propto [R_x^2 + R_y^2]$. The usual Landau result for the free energy per molecule is

$$\begin{aligned} F ={}& \tfrac{1}{2}a_0(T - T_0)(R_x^2 + R_y^2) + \tfrac{1}{3}b(R_y^3 - 3R_x^2R_y)\\ &+ \tfrac{1}{4}c(R_x^2 + R_y^2)^2 + \mathcal{H}_E + \mathcal{H}_{RT}\,. \end{aligned} \tag{16}$$

Here it has been assumed that strain order parameters (e_4, e_5, e_6, e_7) and orientational order parameters (R_x, R_y) in the neighborhood of the phase transition are sufficiently small that an expansion of the form (16) is still valid. We thus expect that third order contributions to F are small, so that the transition is nearly second order. The entire temperature depencence has been included in the term quadratic in R_x and R_y. Temperature dependent quadratic terms can arise either from the entropy (7) or the rotational energy (10); it is actually likely that both contribute to this phenomenological description. Coefficients b, c, ..., the elastic constants $c_{\rho\sigma}^0$, and rotation–translation coupling coefficients A, B, C, D, ... are assumed to be temperature independent in the neighborhood of the phase transition. It is expected that $T_0 < 0$, as is the case for the alkali cyanides.[19,20] It follows that for $a_0 > 0$ and $c > 0$, one must have $b < 0$ if the $\mathcal{H}_R$ terms alone are to stabilize the distorted structure with $(R_x, R_y) \neq 0$. For $b = 0$ the minimum in orientational energy would always be at $(R_x, R_y) = 0$ if $\mathcal{H}_R$ alone were considered. Introduction of the coupling trrms in $\mathcal{H}_{RT}$ raises the transition temperature by producing indirect orientation dependent triazine–triazine interactions, mediated by the lattice, which add considerably to the direct interactions contained in $\mathcal{H}_R$. It should be noted that the present mean field treatment neglects correlations such as

$$\langle R_x^2\rangle - \langle R_x\rangle^2 \ \text{and}\ \langle R_y^2\rangle - \langle R_y\rangle^2\ .$$

At 200 K an estimate of the rms angular displacements for rotations about the x and y axes is about 6°. Hence, in the transition region, $\langle R_x^2\rangle$ and $\langle R_y^2\rangle$ may actually differ considerably from $\langle R_x\rangle^2$ and $\langle R_y\rangle^2$.

It is well known that the crystal develops three domains below T_c ("triple twinning").[4,13] The three domains correspond to molecular rotations

$$R_y\ ,\quad -\tfrac{1}{2}R_y + \frac{\sqrt{3}}{2}R_x\ ,\quad -\tfrac{1}{2}R_y - \frac{\sqrt{3}}{2}R_x\ ,$$

and the strains

$$e_5\ ,\quad -\tfrac{1}{2}e_5 + \frac{\sqrt{3}}{2}e_4\ ,\quad -\tfrac{1}{2}e_5 - \frac{\sqrt{3}}{2}e_4\ ,$$

as well as

$$e_7\ ,\quad -\tfrac{1}{2}e_7 + \frac{\sqrt{3}}{2}e_6\ ,\quad -\tfrac{1}{2}e_7 - \frac{\sqrt{3}}{2}e_6\ ,$$

respectively. We can, however, without loss of generality concentrate on domains in which the order parameters are simply R_y, e_5, and e_7.

Considering these order parameters only, the free energy (16) reduces to

$$F = \tfrac{1}{2}a_0(T - T_0)R_y^2 + \tfrac{1}{3}bR_y^3 + \tfrac{1}{4}cR_y^4 + \tfrac{1}{2}c_{44}^0e_5^2 + \frac{1}{2}\,\frac{c_{11}^0 - c_{12}^0}{2}\,e_7^2$$

$$+ c_{14}^0 e_5 e_7 - A e_5 R_y + \tfrac{1}{2} C e_5 R_y^2 + \tfrac{1}{2} E e_5^2 R_y - \tfrac{1}{4} H e_5^2 R_y^2$$
$$+ B e_7 R_y - \tfrac{1}{2} D e_7 R_y^2 - \tfrac{1}{2} G e_7^2 R_y + \tfrac{1}{4} I e_7^2 R_y^2 - J e_5 e_7 R_y + \cdots \ . \tag{17}$$

Equilibrium values of R_y, e_5, and e_7 are determined by the conditions

$$\frac{\partial F}{\partial R_y} = 0 \ , \quad \frac{\partial F}{\partial e_5} = 0 \ , \quad \frac{\partial F}{\partial e_7} = 0 \ . \tag{18}$$

Since all order parameters are of the same symmetry type, E_g, it is a matter of taste as to which one of the three should be used as the basic order parameter of the system. We expect that solutions to Eqs. (18) have the general form

$$R_y = \sum_{nm} \alpha_{nm} e_5^n e_7^m \ . \tag{19}$$

We choose to express R_y in terms of e_5 and e_7, thus defining e_5 and e_7 as the main order parameters for the system.

It is seen from the from of the elastic energy density (9) that elastic constant c_{44}^0 corresponds to the strain e_5 and elastic constant $\frac{1}{2}(c_{11}^0 - c_{12}^0)$ corresponds to the strain e_7. Which elastic constant actually approaches zero fastest, as the temperature is lowered, depends on the values of the coefficients of the rotation–translation coupling (14). These are at present unknown for triazine. On the basis of experimental evidence,[12,13] we assume that $c_{44}^0 < \frac{1}{2}(c_{11}^0 - c_{12}^0) < c_{14}^0$. This assumption is consistent with the observation that the phase transition is accompanied by a softening of the c_{44}^0 elastic constant.[13]

Equating equal powers of e_5 and e_7 in Eq. (18) allows one to determine the coefficients α_{nm}. The first few are

$$\alpha_{10} = \frac{A}{a_0(T - T_0)} \ , \tag{20}$$

$$\alpha_{01} = -\frac{B}{a_0(T - T_0)} \ , \tag{21}$$

$$\alpha_{20} = -\frac{bA^2}{[a_0(T - T_0)]^3} - \frac{CA}{[a_0(T - T_0)]^2} - \frac{E}{2a_0(T - T_0)} \ . \tag{22}$$

From the data of Smith and Rae,[12] as shown in Fig. 3, one can conclude that the strain component e_7 is very much smaller than e_5. Using Eq. (19), we can write the free energy (17) in the following form for the case $e_5 \gg e_7$:

$$F = \tfrac{1}{2} c_{44}^* e_5^2 + \tfrac{1}{3} b' e_5^3 + \tfrac{1}{4} c' e_5^2 + \cdots \ , \tag{23}$$

in which, keeping only terms to order e_5^4,

$$\tfrac{1}{2} c_{44}^* = \tfrac{1}{2} c_{44}^0 + \tfrac{1}{3} a_0 (T - T_0) \alpha_{10}^2 - A\alpha_{10} \ , \tag{24}$$

$$b' = 3[a_0(T - T_0)\alpha_{10}\alpha_{20} + \tfrac{1}{3} b \alpha_{10}^3 - A\alpha_{20} + \tfrac{1}{2} C \alpha_{10}^2 + \tfrac{1}{2} E\alpha_{10}] \ , \tag{25}$$

$$c' = 4[\tfrac{1}{2} a_0 (T - T_0)(\alpha_{20}^2 + 2\alpha_{10}\alpha_{30}) + b\alpha_{10}^2 \alpha_{20}$$
$$+ \tfrac{1}{4} c \alpha_{10}^4 - A\alpha_{30} + C\alpha_{10}\alpha_{20} + \tfrac{1}{2} E\alpha_{20} - \tfrac{1}{4} G\alpha_{10}^2] \ . \tag{26}$$

Coefficients c_{44}^*, b', and c' are in general temperature dependent.

Suppose the strain e_5 is imposed on the crystal. The molecular rotation coordinate R_y will follow almost immediately to essentially the static equilibrium value. This is due to the rotation–translation coupling and results in an effective (adiabatic) elastic constant c_{44}^{eff}. Having expressed R_y in terms of the strain components by Eq. (19), the effective elastic constant is simply

$$c_{44}^{\text{eff}} = \partial^2 F / \partial e_5^2 \ . \tag{27}$$

Equation (27) gives to order e_5^2

$$c_{44}^{\text{eff}} = e_{44}^* + 2b' e_5 + 3c' e_5^2 \ , \tag{28}$$

with

$$c_{44}^* = c_{44}^0 \, \frac{T - T_0'}{T - T_0} \ , \tag{29}$$

and

$$T_0' = T_0 + \frac{A^2}{a_0 c_{44}^0} \ . \tag{30}$$

The transition temperature T_c is determined from

$$F\big|_{T=T_c} = 0 \ , \quad \frac{\partial F}{\partial e_5}\bigg|_{T=T_c} = 0 \ . \tag{31}$$

Results for the transition temperature are

$$T_c = \frac{T_0' - \xi T_0}{1 - \xi} \ , \tag{32}$$

with

$$\xi = \frac{c_{44}^{\text{eff}}(T_c)}{c_{44}^0} = \frac{2}{9} \, \frac{b'^2}{c_{44}^0 c'}\bigg|_{T=T_c} \ . \tag{33}$$

Since it is expected that c', $\xi > 0$ and it has been assumed that $T_0 < 0$, the inequality $T_c > T_0'$ holds. It follows from Eq. (28) together with Eqs. (21) and (24) that the transition occurs at a temperature above T_0', at which point c_{44}^* is expected to vanish. Only if $b' = 0$ does $T_c = T_0'$ obtain.

In the neighborhood of the transition one can approximate b' and c', as given by Eqs. (25) and (26), by their values at T_c. One then obtains the usual result for the order parameter in the case of a first order transition:

$$e_5(T) = \tfrac{3}{4} e_5(T_c) \left[1 + \left(1 - \frac{8}{9} \, \frac{T_c - T_0}{T - T_0} \, \frac{T - T_0'}{T_c - T_0'} \right)^{1/2} \right] \tag{34}$$

for $T \le T_c$ and zero for $T > T_c$. Here $e_5(T_c) = -\frac{2}{3}(b'/c')/T_c$. Since we expect that $b' < 0$ and $c' > 0$, there is a discontinuity $e_5(T_c)$ in the strain order parameter e_5 at the transition, and the transition is first order. The discontinuity disappears if the third order terms vanish, i.e., if $b' = 0$. Then the transition becomes second order and the strain order parameter has the usual form

$$e_5(T) = \left(\frac{c_{44}^0}{c'} \, \frac{T_0' - T}{T - T_0} \right)^{1/2} \quad (b' = 0) \ . \tag{35}$$

We have fit a temperature dependence of the type (34) to the observed temperature dependence of the lattice strain, as measured by Smith and Rae.[12] A least squares fit of Eq. (34) to these data is shown in Fig. 3.

The actual temperature dependences of b' and c' may be approximated by Eqs. (25) and (26), with all expansion coefficients α_{nm}, except α_{10}, set equal to zero.

The result then is

$$e_5(T)=C_1(T-T_0)\left[1+\left(1-C_2\,\frac{(T-T_0)(T-T_0')}{T_0'-T_0}\right)^{1/2}\right] \qquad (36)$$

for $T\leq T_c$ and zero for $T>T_c$. Here C_1 and C_2 are constants. As shown in Fig. 3, Eq. (36) fits the data of Smith and Rae quite well. The least-squares parameters are $T_0'=193$ K, $T_0=-759$ K, $C_1=3.19\times10^{-5}$, $C_2=0.189$. The large negative value for T_0 confirms our earlier predictions, and is consistent with observations for other ferroelastic phase transitions.[19–33] The improvement over a simple $(T_c-T)^{1/2}$ power law is evident from Fig. 3. Also, the present study of triazine tends to confirm earlier warnings concerning possible non-mean field behavior. In this case we must also caution with the statement that "the observation of a critical-like exponent for the behavior of the long-range order parameter does not, in itself, imply critical behavior."

A classification of the different types of elastic phase transitions in three dimensional crystals has been given by Folk, Iro, and Schwabl.[17] This classification is concerned with transitions for which the order parameter is a strain component and the soft mode is an acoustic phonon. Although these discussions are mainly concerned with second order transitions, they can be applied to transitions which are weakly first order, as is the case for triazine.

The anisotropy of crystals implies that the softening of the acoustic phonons is restricted to subsectors of the wave vector space which are either one- ($m=1$) or two dimensional ($m=2$). It is found that for one-dimensional soft sectors in q space the usual dynamical scaling holds. For two-dimensional soft sectors renormalization group studies indicate that classical critical behavior is modified by logarithmic correction.

Folk *et al.*[17] give KCN, NaCN, and triazine as examples of $m=2$ behavior. However, an examination of the dynamical matrix for acoustic phonons of triazine, as given in Appendix B, shows only $m=1$ soft acoustic modes. Thus, deviation from mean field behavior in the case of triazine may not be so simply rationalized.

In the high temperature phase, where $e_5=0$, the effective elastic constant is c_{44}^*, as given by Eq. (29). This is the same temperature dependence as was found for the elastic constant c_{44} in KCN.[19,20] It is seen that c_{44}^* vanishes at $T=T_0'$. Since, in general $T_c>T_0'$, with T_0 negative, c_{44}^{eff} will reach its lowest value at $T=T_c$, rather than at T_0'. The value of c_{44}^{eff} at the transition is

$$c_{44}^{\text{eff}}\big|_{T=T_c}=c_{44}^0\,\frac{T_c-T_0'}{T_c-T_0}\;.$$

The qualitative behavior of c_{44}^{eff} as a function of temperature is sketched in Fig. 4. No discontinuity in c_{44}^{eff} is predicted at $T=T_c$. The effective elastic constant will only vanish at T_c if the third order coefficient b' vanishes.

In a similar fashion one can find the temperature dependence of the shear elastic constant $\frac{1}{2}(c_{11}-c_{12})$. By keeping terms in the free energy Eq. (17) proportional to e_7^2

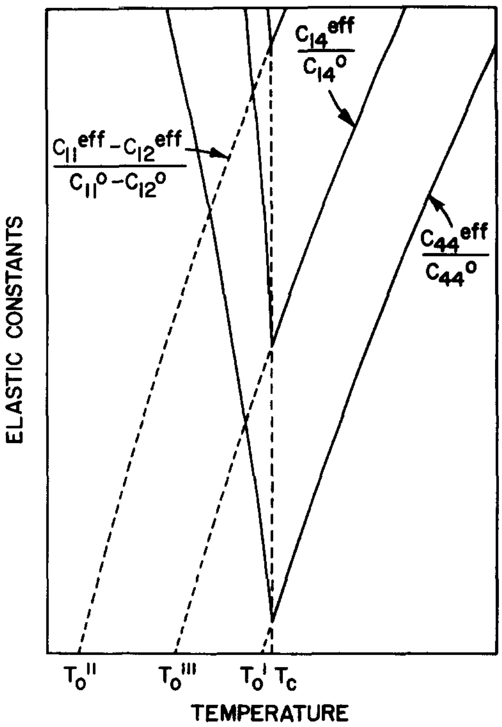

FIG. 4. The predicted behavior of the elastic constants c_{44}, $\frac{1}{2}(c_{11}-c_{12})$, and c_{14} as functions of temperature.

$$F=\tfrac{1}{2}(c_{11}^*-c_{12}^*)e_7^2+\tfrac{1}{2}b''e_5e_7^2+\tfrac{1}{2}c''e_5^2e_7^2\,, \qquad (37)$$

where

$$\tfrac{1}{2}(c_{11}^*-c_{12}^*)=\tfrac{1}{2}(c_{11}^0-c_{12}^0)+\tfrac{1}{2}a_0(T-T_0)\alpha_{01}^2+B\alpha_{01}\,. \qquad (38)$$

The coefficients b'' and c'' are in general temperature dependent and have a form similar to Eqs. (25) and (26) The effective elastic constant is determined from

$$\tfrac{1}{2}(c_{11}^{\text{eff}}-c_{12}^{\text{eff}})=\partial^2F/\partial e_7^2\,. \qquad (39)$$

The result is

$$\tfrac{1}{2}(c_{11}^{\text{eff}}-c_{12}^{\text{eff}})=\tfrac{1}{2}(c_{11}^*-c_{12}^*)+b''e_5+c''e_5^2\,. \qquad (40)$$

The shear elastic constant above T_c, where $e_5=0$, is given by

$$\tfrac{1}{2}(c_{11}^*-c_{12}^*)=\tfrac{1}{2}(c_{11}^0-c_{12}^0)\,\frac{T-T_0''}{T-T_0}\quad , \qquad (41)$$

with

$$T_0''=T_0+\frac{2B^2}{a_0(c_{11}^0-c_{12}^0)}\;. \qquad (42)$$

A sketch of the temperature dependence of $\frac{1}{2}(c_{11}^{\text{eff}}-c_{12}^{\text{eff}})$ is given in Fig. 4. For the case of bilinear coupling only, that is, all coefficients in the rotation–translation coupling Eq. (16) except A and B are set equal to zero, the low and high temperature solutions for $\frac{1}{2}(c_{11}^{\text{eff}}-c_{12}^{\text{eff}})$ can be shown to match as indicated in the figure.

To determine the temperature dependence of the elastic constant c_{14}^{eff} one expands the free energy in terms of $e_5^ne_7$:

$$F=c_{14}^*e_5e_7+\tfrac{1}{2}b'''e_5^2e_7+\tfrac{1}{3}c'''e_5^3e_7\,. \qquad (43)$$

Here

$$c_{14}^{*}=c_{14}^{0}+a_0(T-T_0)\alpha_{10}\alpha_{01}-A\alpha_{01}+B\alpha_{10}\ , \tag{44}$$

and the coefficients b''' and c''' can again be determined in the same manner as for Eqs. (25) and (26). The effective elastic constant is

$$c_{14}^{\text{eff}}=\partial^2F/\partial e_5 e_7\ , \tag{45}$$

which yields

$$c_{14}^{\text{eff}}=c_{14}^{*}+b'''e_5+c'''e_5^2\ , \tag{46}$$

with

$$c_{14}^{*}=c_{14}^{0}\ \frac{T-T_0'''}{T-T_0}\quad , \tag{47}$$

and

$$T_0'''=T_0-AB/a_0c_{14}^{0}\ . \tag{48}$$

The qualitative behavior of c_{14}^{eff} is also shown in Fig. 4. As is the case for the shear elastic constants c_{44}^{eff} and $\frac{1}{2}(c_{11}^{\text{eff}}-c_{12}^{\text{eff}})$, c_{14}^{eff} also shows anomalous behavior in the vicinity of the transition.

The effective elastic constants can also be calculated using the approach of Slonczewski and Thomas.[30] The results are basically the same as those given above, but have a somewhat different form. Details are given in Appendix C.

VI. LIBRATIONAL FREQUENCIES

An estimate of the $\mathbf{q}=0$ rotational frequencies for molecular librations about the x and y axes can be found from

$$\left.\frac{\partial^2\mathcal{H}}{\partial R_i\partial R_j}\right|_{e_\rho=\text{const}}-I\omega_i^2\delta_{ij}=0\qquad(i,j=x,y)\ , \tag{49}$$

where I is the moment of inertia of the triazine molecule about the x or y axes. For triazine $I_x=I_y=I=\frac{1}{2}I_z$. In Eq. (49) one uses the total energy $\mathcal{H}$, as given by Eq. (15). The strain components e_ρ are held constant because the lattice strains cannot relax during the period of a librational oscillation. Since Raman scattering measurements involve small but finite wave vectors, the librational modes will to a slight extent mix with the acoustic modes. This coupling is ignored in the present treatment.

For the case of $e_4=e_6=R_x=0$ the off-diagonal terms of Eq. (49) vanish, so that the librational frequencies are just equal to the diagonal terms. The results are

$$I\omega_x^2=\left.\frac{\partial^2\mathcal{H}}{\partial R_x^2}\right|_{e_5=\text{const}}=-a_0T_0-2bR_y+cR_y^2-Ce_5+\tfrac{1}{2}He_5^2\ , \tag{50}$$

and

$$I\omega_y^2=\left.\frac{\partial^2\mathcal{H}}{\partial R_y^2}\right|_{e_5=\text{const}}=-a_0T_0+2bR_y+3cR_y^2+Ce_5-\tfrac{1}{2}He_5^2\ . \tag{51}$$

In the high temperature phase $R_x=R_y=0$ and $e_5=0$, so that $\omega_x^2=\omega_y^2\sim-a_0T_0$. Below T_c, ω_x and ω_y are split according to

$$I(\omega_y^2-\omega_x^2)=4bR_y+2cR_y^2+2Ce_5-He_5^2\ . \tag{52}$$

Whether ω_x or ω_y is larger depends on the signs of the coupling coefficients and perhaps the relative contributions of the R_y and e_5 terms. For sodium azide the higher-lying mode was identified with A_g [libration in the $(xz)_M$ plane or R_y] and the lower-lying mode with B_g [libration in the $(yz)_M$ plane or R_x].[31] This splitting is in qualitative agreement with the Raman spectrum of the rotary E_g mode for $T<T_c$.[5] To lowest order $R_y\propto e_5$; if $b\neq0$ and/or $C\neq0$, then the splitting of the E_g rotary lattice can be approximated as

$$\Delta\omega=|\omega_y-\omega_x|\propto e_5\ .$$

Hence, the frequency splitting $\Delta\omega$ is proportional to the order parameter but only to lowest order where the latter is small. Therefore, care should be taken in defining a proper temperature range when a splitting of the librational frequencies is directly identified as the order parameter, as has been done for other systems.[32,2a]

Translational lattice mode frequencies and intramolecular vibrational frequencies depend on the crystal environment of each molecule. Because that environment changes at the phase transition, a splitting of some triazine intramolecular modes results.[5-7] The change in symmetry at the structural phase transition is also reflected in the NQR spectra.[8] In this latter case splittings of resonances in the monoclinic phase are expected to be proportional to the order parameter. Splitting in the low temperature phase is found to be well described by a $(T_c'-T)^{1/2}$ law, with $T_c'=200.8$ K. Only very close to $T_c=198.8$ are deviations from the Landau theory with $\beta=\frac{1}{2}$ observed.[8,14]

The NQR measurements indicate that triazine undergoes molecular reorientation about the threefold axis only at high temperature. The activation enthalpy is quite large, $\Delta H\cong14$ kcal/mol.[8] Although the rather well-localized librational motion about the threefold axis is no doubt affected by the ferroelastic transition, the R_z motion does not couple to the strains in a bilinear fashion, as does the (R_x, R_y) rocking motion. Some form of coupling between (e_4, e_5) and R_z must take place in higher order, e.g., $R_ze_4e_5$, $R_z^2(e_4^2+e_5^2)$, etc. Details of the coupling between translational, intramolecular, and reorientational motions with the changing lattice environment near the phase transition remain to be elucidated.

VII. CONCLUSIONS

This study has presented a relatively complete theoretical description of the *sym*-triazine trigonal–monoclinic phase transition in the mean field Landau limit. The transition is seen to arise from a coupling between shear (transverse) acoustic modes associated with elastic constant $c_{44}^0(e_4, e_5)$ and molecular rotations out of the basal plane (R_x, R_y). The Hamiltonian of the crystal is found to consist of three contributions: orientational, elastic, and the rotation–translation coupling. This coupling leads to an indirect orientation-dependent interaction between triazine molecules. This indirect coupling is added to the direct orientation dependent triazine–triazine interactions which consist mainly of electronic overlap and octupole–octupole contributions. It is this indirect interaction which overcomes a very strong orienting crystal field and brings about the structural transformation.

Within the Landau mean field theory, expansion of the free energy of the crystal has been written in terms of the strains $(e_4, e_5, e_6, e_1 - e_2)$ and the rotations (R_x, R_y). In the neighborhood of the transition all expansion coefficients, except the one for the $(R_x^2 + R_y^2)$ orientational term, are assumed to be temperature independent. For this term the usual $a_0(T - T_0)$ dependence is used. This temperature dependence of the quadratic term in the free energy expansion can arise from either or both of the following contributions: an effective orientational field experienced by a single molecule in the environment of of its neighbors, which is temperature dependent, and an entropy contribution due to a change in the orientational distribution function.

The specific heat anomaly associated with the structural transformation in triazine is similarly made up from the following contributions: an orientational ordering term, as considered in Sec. III, and a lattice dynamical term. The lattice dynamical specific heat contribution is a function of the Debye temperature of the crystal. One would expect an anomaly in the specific heat to be due to both rotational ordering (entropy terms) and the softening of the transverse acoustic phonon velocities v_{TA} in certain directions in the Brillouin zone.

If the lattice dynamical terms dominate the orientational entropy contributions, the transition might be classified "displacive" rather than "order disorder." This is probably the case for triazine since the extent of the disorder in the high temperature phase seems to be small. The details of the temperature dependence of the orientational distribution function remain to be worked out.

The structural transformation in triazine is found to be weakly first order. The elastic constants c_{44}, $\frac{1}{2}(c_{11} - c_{12})$, and c_{14} all exhibit a strong temperature dependence near the transition, but do not actually vanish because of the first order character of the transition. The elastic constant c_{44} shows the strongest temperature anomaly. A comparison of the predicted temperature dependence of the strain order parameter e_5 with experiment indicates an improvement over a simple $(T - T_c)^{1/2}$ mean field power law. This is mainly due to the cubic term in the free energy which produces a discontinuity of the order parameter at the transition.

Based on the coupled Hamiltonian, librational frequencies are calculated at constant values of the strains. These frequencies are different for R_x and R_y librations. with a first order splitting proportional to the order parameter for the transition e_5. However, e_5 must be small for this approximate relationship to hold.

APPENDIX A

I. Elastic constant matrix

In the coordinate system of Fig. 1, nonzero elements of the elastic constant matrix for $D_{3d}(\bar{3}m)$ symmetry are

	1 xx	2 yy	3 zz	4 yz	5 zx	6 xy
1 xx	c_{11}	c_{12}	c_{13}		c_{14}	
2 yy	c_{12}	c_{11}	c_{13}		$-c_{14}$	
3 zz	c_{13}	c_{13}	c_{33}			
4 yz				c_{44}		$-c_{14}$
5 zx	c_{14}	$-c_{14}$			c_{44}	
6 xy				$-c_{14}$		$\frac{1}{2}(c_{11} - c_{12})$

Here we employ the Voigt notation where

$$c_{\rho\sigma} = c_{\alpha\beta\gamma\lambda} ,$$

$$e_\rho = e_{\alpha\beta} , \quad \alpha = \beta = \rho ,$$

$$e_\rho = e_{\alpha\beta} + e_{\beta\alpha} , \quad \alpha \neq \beta , \quad \rho = q - \alpha - \beta .$$

APPENDIX B

I. Acoustic dynamical matrix

In the coordinate system of Fig. 1 the dynamical matrix of acoustic modes for $D_{3d}(\bar{3}m)$ symmetry is

$$M_{\alpha\beta}(\mathrm{q})$$

$$\begin{array}{c|ccc}
\alpha \backslash \beta & x & y & z \\
x & c_{11}q_x^2 + \frac{1}{2}(c_{11} - c_{12})q_y^2 + c_{44}q_z^2 + 2c_{14}q_xq_z & \frac{1}{2}(c_{11} + c_{12})q_xq_y - 2c_{14}q_yq_z & (c_{13} + c_{14})q_yq_z - 2c_{14}q_xq_y \\
y & & \frac{1}{2}(c_{11} - c_{12})q_x^2 + c_{11}q_y^2 + c_{44}q_z^2 - 2c_{14}q_xq_z & (c_{13} + c_{14})q_xq_z + c_{14}(q_x^2 - q_y^2) \\
z & & & c_{44}(q_x^2 + q_y^2) + c_{33}q_z^2
\end{array}$$

The diagonalization of the matrix $M_{\alpha\beta}(\mathrm{q})$ yields the following eigenvalues for q along the following symmetry directions:

$$\mathrm{q} = [0\ 0\ \zeta]$$

$$\rho\omega_{\mathrm{LA}}^2 = c_{33}\zeta^2 , \tag{B1}$$

$$\rho\omega_{\mathrm{TA}}^2 = c_{44}\zeta^2\ ; \tag{B2}$$

$$\mathbf{q} = [\xi\ 0\ 0]\ ,$$

$$\rho\omega_{\mathrm{LA}}^2 = c_{11}\xi^2\ , \tag{B3}$$

$$\rho\omega_{\mathrm{TA}}^2 = \tfrac{1}{2}\xi^2\left([\tfrac{1}{2}(c_{11}-c_{12})+c_{44}] \pm\{[\tfrac{1}{2}(c_{11}-c_{12})+c_{44}]^2 - 4[\tfrac{1}{2}(c_{11}-c_{12})c_{44}-c_{14}^2]\}^{1/2}\right)\ , \tag{B4}$$

$$\mathbf{q} = [0\ \eta\ 0]\ ,$$

$$\rho\omega_{\mathrm{LA}}^2 = \tfrac{1}{2}(c_{11}-c_{12})\eta^2\ ,$$

$$\rho\,\omega_{\mathrm{TA}}^2 = \tfrac{1}{2}\eta^2\{(c_{11}+c_{44}) \pm [(c_{11}-c_{44})^2+4c_{14}^2]^{1/2}\}\ . \tag{B5}$$

APPENDIX C

I. Effective elastic constants

The effective elastic onstants can be calculated from[29]

$$c_{\rho\sigma}^{\mathrm{eff}} = c_{\rho\sigma}^0 - \sum_{kl} \frac{\partial^2 F}{\partial e_\rho\,\partial R_k} S_{kl} \frac{\partial^2 F}{\partial R_l\,\partial e_\sigma}\ , \tag{C1}$$

where the matrix S_{kl} satisfies

$$\sum_l S_{kl} \frac{\partial^2 F}{\partial R_l\,\partial R_m} = \delta_{km}\ . \tag{C2}$$

For the case $e_4 = e_6 = R_x = 0$ and $e_7 \ll e_5$ one finds

$$c_{44}^{\mathrm{eff}} = c_{44}^0 - \frac{A'^2}{a'}\ ,$$

$$\frac{c_{11}^{\mathrm{eff}} - c_{12}^{\mathrm{eff}}}{2} = \frac{c_{11}^0 - c_{12}^0}{2} - \frac{B'^2}{a'}\ ,$$

$$c_{14}^{\mathrm{eff}} = c_{14}^0 + \frac{A'B'}{a'}\ , \tag{C3}$$

where

$$A' = A - CR_y - Ee_5 + He_5R_y\ ,$$

$$B' = B - DR_y - Je_5\ ,$$

$$a' = a_0(T-T_0) + 2bR_y + 3cR_y^2 + Ce_5 - \tfrac{1}{2}He_5^2\ . \tag{C4}$$

An expansion of Eqs. (C3) in terms of e_5 yields the corresponding relations in Sec. IV.

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