

Brillouin-scattering study of the elastic constants of phenothiazine through the phase transition

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It has been proposed that single crystals of phenothiazine undergo a proper ferroelastic phase transition: $Pnma(D_{2h}) \rightarrow P2_1/c(C_{2h})$. This premise is in conflict with Brillouin-scattering studies from both quasi- and high-symmetry longitudinal and transverse acoustic modes reported here. The C_{55} elastic constant of phenothiazine as an orthorhombic crystal at ambient conditions shows no temperature dependence. The inelastic, light-scattering spectra support an order-disorder phase transition; no significantly unstable acoustic phonons were observed through the phase transition. Laser diffraction from structural domains reveals that the crystal is polysynthetically twinned above and below T_c . At room temperature, domain walls are made indistinct by disorder but become visible as the sample is cooled. Stress-strain hysteresis below T_c is attributed to a ferrobielastic effect.

I. INTRODUCTION

Phenothiazine is a nonplanar, tricyclic, aromatic compound with the structure shown in Fig. 1. In crystalline form, it is known to undergo a structural phase transition (SPT) that results in the generation of visible striae within the crystal.¹ Speculations on the microscopic origins of the SPT and the formation of such striae have become a significant area of controversy. Interest in phenothiazine was stimulated by the conjecture of Nakayama and co-workers¹⁻³ that, upon cooling, a strain forms spontaneously within the crystal as the result of a structural change from an orthorhombic to a monoclinic lattice. They also observed that striae arise from lamellar domains of the low-temperature phase of phenothiazine, which can be altered by the application of a small tensile stress. Such domains persist until a different stress is applied. Hysteretic behavior is characteristic of ferroelasticity. Nevertheless, domain formation and even domain switching can be associated with several other phenomena such as order-disorder behavior, polysynthetic twinning and ferrobielasticity.⁴ Ferroelasticity has been observed only in a small number of organic crystals, and, as yet, has not been unequivocally determined for the SPT in phenothiazine.

To date, one ultrasound and a number of Raman and Brillouin studies have been used to examine the role of the acoustic and optical phonons in the SPT of phenothiazine in light of possible ferroelastic behavior.^{1-3,5-7} Although the evidence is conflicting, instabilities in the e_3 shear and the totally symmetric e_3 strain have been associated with the SPT.^{3,6} These shear and strain instabilities are consistent with a true ferroelastic SPT, which requires an orthorhombic to a monoclinic structural transition and the softening of a B_{2u} acoustic mode.⁴ However, the light-scattering data are not consistent with order-disorder behavior.^{2,6} In addition, recent NMR studies point to a phase transition that is governed by strong rotation-translation coupling rather than just by an overdamping of an acoustic mode.⁸ The low-energy, Raman-active modes display a significant

amount of anharmonicity through the phase transition.

Conclusions made from the light-scattering studies are problematic when characteristics of high-purity single crystals of phenothiazine are considered. The reported relative magnitudes of the C_{11} , C_{22} , and C_{33} elastic constants are inconsistent with the macroscopic properties of the crystal (the room-temperature unit cell is designated: $c > b > a$ following the convention of Nakayama and Ishii²). The relative magnitudes of these compressional elastic constants are assigned as $C_{33} > C_{22} > C_{11}$ based on earlier Brillouin-scattering data.⁶ This result, however, is in conflict with the observation that phenothiazine is readily cleavable into (00n) platelets. Thus the compressive elastic constant perpendicular to the (001) plane, C_{33} , should be significantly smaller than those within the plane, C_{22} and C_{11} . Lattice-dynamic calculations, based on atom-atom potentials, also describe a crystal that is more compliant (small elastic constant) along the c axis rather than along the a or b axes of the unit cell. A significantly smaller phonon velocity was calculated for q_c than for q_a or q_b .⁹

To date, five separate crystallographic investigations have been performed on phenothiazine; each has yielded a different, albeit not necessarily consistent, description of the crystal structure. An early x-ray diffraction description of the room-temperature crystal structure by Bell *et al.*¹⁰ was of a noncentrosymmetric monoclinic $P2_1(C_s)$ structure. All other crystallographic studies,

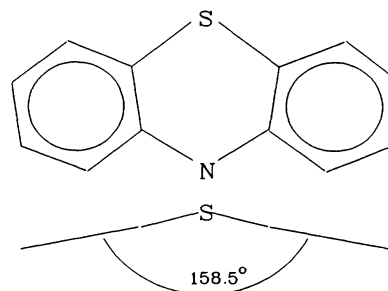


FIG. 1. Molecular structure of phenothiazine.

however, describe lattices with inversion symmetry: a monoclinic $P2_1/c$ (C_{2h}),¹¹ an orthorhombic $Pnma$ (D_{2h}),^{11,12} a polysynthetically twinned or disordered $P2_1/c$ (C_{2h}),¹³ or a disordered $Pnma$ (D_{2h}) (Ref. 14) structure. The phenothiazine crystal grows with either a needle or platelike habit but polymorphic distinction is not clearly evident.¹³ Van de Waal and Feil,¹³ who first observed that phenothiazine undergoes a phase transition, believe that all the previous room-temperature structural studies are inaccurate because of molecular disorder along the c axis and their structure reflects a correction for this. They also performed the only low-temperature structural study, and concluded that the low-temperature lattice contained inversion symmetry. However, a weak pyroelectric effect observed in this study and by Wood, McCale, and Williams¹¹ at 90 K would indicate a noncentrosymmetric lattice and a probable $P2_1(C_s)$ low-temperature structure.

The formation of striae or domains suggests a change in lattice structure. In accord with Landau theory, a structural transition $Pnma(D_{2h})$ to $P2_1/c(C_{2h})$, as previously proposed, should result from the spontaneous generation of an e_s strain and an unstable B_{2u} acoustic mode. However, ambiguity concerning the lattice structure has resulted in a number of conflicting descriptions of the phase transition. Three specific mechanisms for the phase transition have emerged: order-disorder,¹³ overdamping of an optical libration,^{14,15} or a ferroelastic structural change.

In all cases but that of Sircar, Mishra, and Gupta,¹⁵ who assumed a $P2_1(C_s)$ structure, there are reported experimental efforts to verify lattice type at room temperature. Nakayama and Ishii,² in particular, regard the Raman-scattering tensor for phenothiazine as consistent with an orthorhombic lattice above T_c and a monoclinic lattice below T_c . To obtain their result, they assume and require than an observed low-energy 22-cm^{-1} optic mode be a molecular butterfly mode. As expected for a molecular mode, this mode displays no significant dependence on changes in temperature or pressure. However, a molecular assignment has yet to be confirmed. An optical mode at 49 cm^{-1} has been observed in the vapor-phase Raman spectrum,⁷ but for a vibrational motion of this type, a shift to higher energy in the solid state would be expected because of the constraining intermolecular forces. Lattice-dynamic calculations also suggest that a 22-cm^{-1} (B_{2u}) vibration is acoustic.⁸ The calculations further suggest that if a butterfly mode does exist it would occur above 80 cm^{-1} . The method of crystal growth also plays a significant role on the phase transition; T_c 's are recorded near 220 K for solution grown samples^{13,15} and 240 ± 2 K for vapor and boule grown crystals.^{1-3,6,16}

Many of the conclusions drawn to date were necessitated by the experimental difficulties in obtaining sufficient data for a complete set of elastic constants in such low-symmetry lattices. Because of calculational and experimental advances in our laboratory, we are able to report the results of Brillouin scattering involving 36 different acoustic-phonon modes of single crystals of phenothiazine, six of which are associated with the high-symmetry,

true transverse, and true longitudinal wave vectors parallel to the a and b axes and three with wave vectors within 7° of the high-symmetry c axis. All measurements were made using a four-circle Brillouin spectrometer¹⁷ and corrections were made for the temperature dependence and anisotropy of the optical indicatrix. In the previous Brillouin-scattering study,⁶ elastic constants were estimated solely from quasitransverse and quasilongitudinal phonon velocities.

The following sections present: (1) a brief description of the theory of Brillouin scattering and the determination of elastic constants with a four circle instrument, (2) a general method for determining the wave vector direction of an acoustic phonon, within an anisotropic crystal, coupled to externally non-normal incident or scattered laser radiation, (3) a detailed discussion of the crystallography of very high-purity phenothiazine and the confusion surrounding the crystal structure, (4) a comparison of the results from our study with the theoretical lattice-dynamical results of Criado,⁹ the macroscopic properties of phenothiazine single crystals and the light-scattering and ultrasound results of Ecolivet *et al.*⁶ and Nakayama, and co-workers,¹⁻³ and finally, (5) a model for the phase transition is proposed.

II. BRILLOUIN SPECTROSCOPY: DETERMINATION OF ELASTIC CONSTANTS

Brillouin scattering is treated extensively in the literature and the paper by Benedeck and Fritsch,¹⁸ and Fabelinskii,¹⁹ Cummins and Schoen,²⁰ and Vacher and Boyer²¹ are particularly relevant. Only a brief summary is presented here.

The frequencies of acoustic phonons are obtained from an equation that describes the Doppler shift of Bragg-diffracted light scattered from a sound wave traveling within a crystal at velocity $V(\hat{q})$ and of frequency $\nu_{\hat{q}}$. To account for optical anisotropy or birefringence, which is usually the case in organic crystal systems, dependence of the refractive indices of the incident and scattered rays, n_i and n_s , respectively, is included. The resulting equation is:

$$\nu_s = \nu_0 \pm \nu_q = \nu_0 \pm \nu_0 \frac{V(\hat{q})}{c} (n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{1/2}, \quad (1)$$

where θ is the forward scattering angle and ν_0 is the frequency of the incident light.

In the long-wavelength approximation, where the acoustic phonons are regarded as sound waves, polarizations and frequencies are related to the elastic constants $C_{\alpha\beta\gamma\delta}$ through the equation of motion

$$\rho \ddot{U}_\alpha = C_{\alpha\beta\gamma\delta} \frac{\partial^2 U_\delta}{\partial r_\beta \partial r_\gamma}, \quad (2)$$

where U_α is the set \hat{u} of molecular displacements. This equation is entirely analogous to the vibrational equation of motion for molecules except now the displacements represent the long-wavelength, elastic continuum.

Using plane-wave solutions, Eq. (2) becomes

$$\rho V(\hat{q})^2 U_\alpha = \Gamma_{\alpha\delta} U_\delta, \quad (3)$$

where ρ is the volume density of the crystal, $V(\hat{q})$ is the phase velocity of the acoustic phonon and

$$\Gamma_{\alpha\delta} = C_{\alpha\beta\gamma\delta} q_\beta q_\gamma. \quad (4)$$

The matrix Γ is symmetric with respect to the interchange of the dummy variables α and β , and q_α and q_β are the direction cosines of the unit vector normal to the plane wave. Three mutually perpendicular directions of vibration are ascribed to a particular direction of propagation.

The frequencies and polarizations of acoustic waves are obtained from the standard secular equation:

$$\det|\Gamma_{\alpha\delta} - \rho V(\hat{q})^2| = 0. \quad (5)$$

If the \hat{q} -dependent phonon eigenfrequencies and eigenvectors are known, the elastic constants can be determined. In low-symmetry crystals an analytical solution to Eq. (5) is only possible with pure vibrations, i.e., those vibrations that occur along directions of high symmetry within the crystal and that are perfectly transverse or longitudinal. Phonons in any other direction usually exhibit mixed characteristics of both. The propagation directions for pure transverse or pure longitudinal phonon modes can be determined²² and tables of them are available.²⁰ These directions are difficult, if not impossible, to experimentally access in low-symmetry molecular crystals.

The number of pure phonons dramatically decreases as the space-group symmetry is lowered. In such cases, unique solutions to Eqs. (3) and (5) become impractical. An analytical approach was developed to circumvent this problem through a least-squares minimization of Eq. (5) using reasonable initial approximations for either the elastic constants or a set of experimental phonon velocities from a sufficiently overdetermined number of propagation directions.²³ The advantage of this method is that it eliminates the need to use purely longitudinal or purely transverse modes. Thus, modes of any arbitrary propagation direction \hat{q} may be utilized and are generally referred to as quasilongitudinal or quasitransverse. The use of the quasimodes eliminates the need for destructive or damaging crystal cutting to obtain the desired faces.

For many low-symmetry crystal systems this method may be the only means to obtain the entire set of elastic constants. There are, however, some unavoidable inconveniences. One is that a large sampling of the different \hat{q} vectors is required to give a good fit, and this requires many measurements. Crystal optics can also become increasingly complicated, especially for non-normal scattering. In addition, in the study of phase transitions and mode softening, it may still be important to observe certain pure modes because of possible strong spatial dispersion of \hat{q} , particularly along high-symmetry directions within the crystal. Ideally, one would like to have a spherical crystal to sample a statistically large number of directions. However, quite reasonable results can be obtained if efforts are made to include as many pure modes as possible and to use enough quasimodes to provide a reasonable statistical sampling of \hat{q} within the crystal.

III. EXPERIMENTAL

A. Purification, crystal growth, and crystallography

Phenothiazine is a pale, yellow solid obtained from the Aldrich Chemical Company at an approximate purity of 98%. It was sublimed at least three times to remove inert material followed by repeated zone refining for further purification.^{24,25} Each of the five stages of the zone refiner used can be regulated to within 0.1°C for long periods of time to prevent excessive heating of the phenothiazine liquidus. Two boules were zone refined for approximately 100 and 200 passes. The resulting purified central section of the boule was off-white. The material was always handled in inert atmospheres.

High-quality single crystals of phenothiazine were subsequently grown by slow sublimation for eight weeks in a glass cell 7.5 cm in diameter and 2.5 cm wide.²⁵ Both crystal habits of needles and platelets were observed. Although phenothiazine usually appears as platelets, a needle-shaped polymorph of phenothiazine was also reported by Bell *et al.*¹⁰ The needle-shaped crystals proved too fragile to handle. Therefore, all experiments were performed on the platelet samples. Typical crystal dimensions were $4 \times 3 \times 1.5$ mm³.

Crystal interfacial angles were measured by optical goniometry. Utilizing the law of rational indices and the orthorhombic structure of McDowell,¹² the differences between the experimental and calculated interfacial angles were less than 0.7%. Similar agreement could not be obtained with the monoclinic structures of Bell *et al.*¹⁰ or van de Waal and Feil.¹³ Thus, the habit is consistent with an orthorhombic structure.

Single-crystal x-ray (Cu_α) analysis was used to further verify the room-temperature axial assignments. Precession x-ray patterns are consistent with an orthorhombic lattice (see Table I). Although the lattice appears orthorhombic from this measurement, the actual space group of the crystal should be regarded as somewhat inconclusive in light of previous, more extensive, x-ray studies. Furthermore, it was not possible to determine if the unit cell contains a center of inversion, although a slight pyroelectric effect was observed at 77 K.

The refractive indices at various temperatures near and

TABLE I. Temperature-dependent refractive indices of phenothiazine at 514.5 nm.

Temperature (K)	n_a	n_b	n_c
295	1.70	2.00	1.79
275	1.69	1.98	1.83
265	1.72	1.93	1.77
255	1.70	1.97	1.75
250	1.71	1.97	1.75
249	1.75	1.97	1.75
248	1.68	1.95	1.73
247	1.68	1.94	1.75
245	1.67	1.94	1.76
240	1.73	1.94	1.75
220	1.79	1.99	1.75

IV. RESULTS

A. Heat of transition

Differential scanning calorimetry (DSC) was used to determine the transition energy of the SPT for phenothiazine crystals grown by sublimation. A Perkin-Elmer model DSC-4 calorimeter was employed with the heat of freezing of water as the standard. The phenothiazine phase transition found at 248 ± 0.5 K was endothermic and reversible with no annealing effects observed after three temperature cycles. The heat of transition for the vapor-grown crystals, 9.3 cal/mol, was considerably smaller than the 47.8 cal/mol reported by Nakayama *et al.*¹ who used a melt-grown specimen. This difference in the heat of transition is significant and probably reflects excess strain energy in the melt-grown sample. This is corroborated by the range of transition temperatures determined in this study, and by previous investigators, which supports a growth method dependence for the SPT.

B. Temperature-dependent Brillouin spectra

More than 1500 spectra were recorded for 12 different phonon wave vectors, or 36 different acoustic-phonon modes, at 11 successive temperatures through the phase transition. Each was determined for four different sets of polarizations of incident and scattered light: V_v , V_h , H_h , and H_v . The designations V and H refer to the polarization vectors of the light incident upon the crystal that are perpendicular and parallel, respectively (or nearly so, depending upon the optical indicatrix of the crystal) to the optical plane of the Brillouin instrument; subscripts v and h refer to polarizations of the scattered light defined in the same manner. At least two different free spectral ranges were recorded for each measurement to determine the order of the Brillouin components. Representative spectra are shown in Figs. 4 and 5. Each spectrum represents the sum of 25 scans; each scan represents the sum of photons scattered from the crystal observed for approximately 7 msec per channel for a total of 1000 channels.

The plots in Fig. 3 display the temperature evolution of all three components of the Brillouin spectrum for the high-symmetry wave vectors along the a , b , and c^* axes. The only way to access the true c -axis wave vector is in the backscattering arrangement from the large plate face of the crystal; c^* is 7° from the actual c axis. Spectra were recorded at temperatures between 295 and 250 K but are not included for clarity and conservation of space. The spectra in Fig. 4 show the possible effect that domain formation may have on select Brillouin components.

C. Elastic constants

The complete set of elastic constants for phenothiazine was determined as described. Because of the uncertainty of the space-group assignment of phenothiazine at temperatures above and below T_c , two sets of elastic constants were calculated based on the orthorhombic and the monoclinic structures associated with phenothiazine.

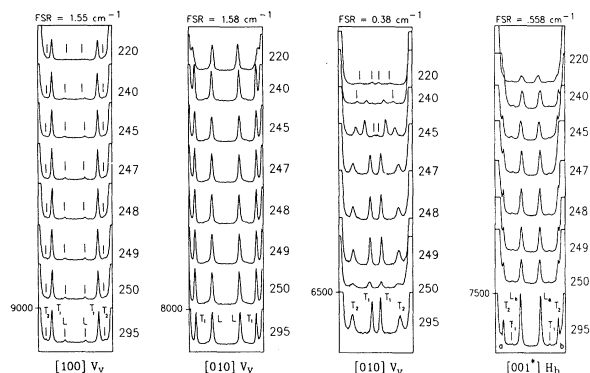


FIG. 3. Temperature evolution of the longitudinal (L), transverse (T_1), and transverse (T_2) Brillouin spectral components for the high-symmetry wave vectors $[100]$ and $[010]$ and the wave vector $[001^*]$ which is within 7° of the high-symmetry $[001]$ wave vector. Absolute temperatures are shown on the right ordinates. The left ordinate shows the intensity as number of counts/sec. Abscissae show the free spectral range. Polarization configurations, defined in Sec. IV B are also indicated.

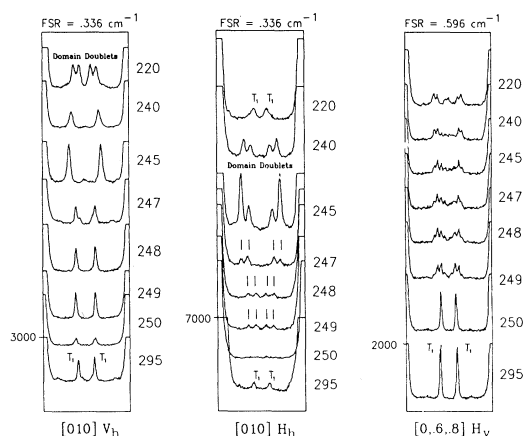


FIG. 4. Effect of structural domain formation on $[010]$ and $[0,0.6,0.8]$ phonon spectra for indicated polarization configurations (Sec. IV B). Absolute temperature (right ordinates), intensity in counts/sec (left ordinates) and free spectral ranges (abscissae) are displayed.

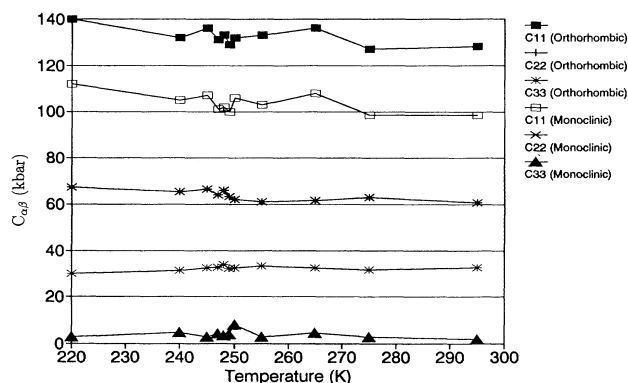


FIG. 5. Temperature evolution of the C_{11} , C_{22} , and C_{33} elastic constants through T_c .

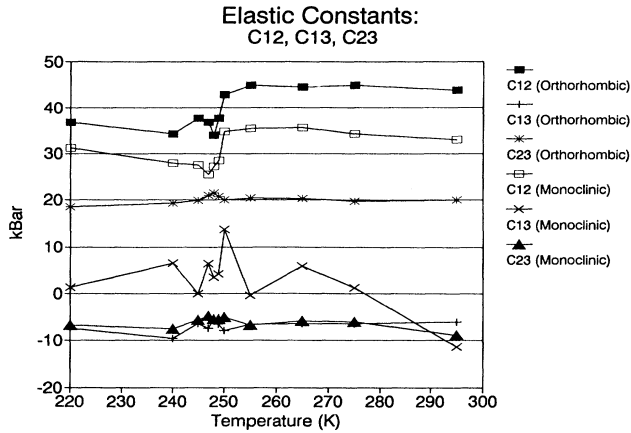


FIG. 6. Temperature evolution of the C_{12} , C_{13} , and C_{23} elastic constants through T_c .

Acoustic-phonon wavevectors were determined using the relation of van de Waal and Feil¹³ ($c > b > a$)

$$a_m \simeq c_0, \quad b_m \simeq a_0, \quad c_m \simeq b_0 + c_0, \quad (6)$$

which correlated the orthorhombic structure of McDowell ($b > c > a$) to a monoclinic unit cell. Although the results of both the precession x-ray study and the optical goniometry support an orthorhombic, room-temperature structure, the inclusion of the monoclinic set of elastic constants is presented because the structure of phenothiazine may actually be a polysynthetically twinned or disordered monoclinic structure or may become monoclinic at low temperature.

The refractive indices recorded at the same temperatures used in the Brillouin experiment were utilized in Eq. (5) to obtain the actual velocities of the acoustic phonons. In previous studies, a temperature-independent set of refractive indices obtained at room temperature was used. Using the actual values of the refractive indices at a given temperature has a significant impact on the elastic constant results. Errors in the experimentally deter-

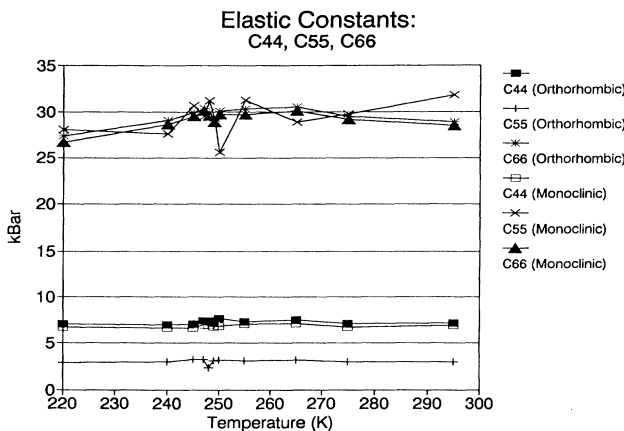


FIG. 7. Temperature evolution of the C_{44} , C_{55} , and C_{66} elastic constants through T_c .

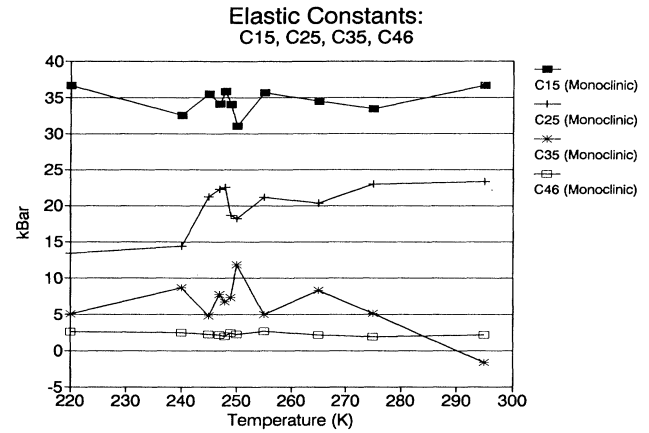


FIG. 8. Temperature evolution of the C_{15} , C_{25} , C_{35} , and C_{46} elastic constants through T_c .

mined set of elastic constants ranging from 15 to 35 % can result by ignoring the temperature dependence of the birefringence. The temperature dependence of the four sets of elastic constants is shown in Figs. 5–8.

D. Intensity measurements of the Brillouin spectra

A comparison in Fig. 9 of the room-temperature Brillouin intensities of the three longitudinal modes for phenothiazine traveling along the high symmetry axes a , b , and c^* , shows an interesting feature. The scattering intensity associated with the longitudinal phonon mode traveling along the a axis is much smaller than that for the longitudinal phonons traveling along the b or c axes. This is shown by the ratios of the integrated intensities I_T/I_L shown in Table II. These indicate disorder occurs along only the a axis and perpendicular to the domain walls observed below T_c . The longitudinal and the quasi-longitudinal modes typically display the greatest frequency shifts and intensities because the restoring forces and changes in dipole moment are generally larger for longitudinal than transverse phonon motions.

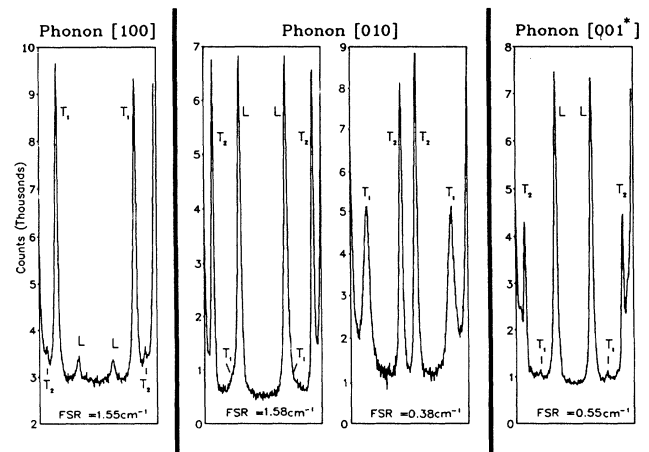


FIG. 9. Spectra of high-symmetry acoustic phonons assuming an orthorhombic lattice with $c > b > a$.

TABLE II. Ratios of integrated intensities for pure acoustic modes of phenothiazine.

Phonon	I_T/I_L
(100) L	1.0
(100) T_1	8.5
(100) T_2	0.14
(010) L	1.0
(010) T_1	0.90
(010) T_2	0.42
(001) L	1.0
(001) T_1	0.02
(001) T_2	0.07

V. DISCUSSION

A. Role of twinning and domains

The diffraction of laser light provides an important method of observing domain formation within single crystals of phenothiazine. Regular laser-light diffraction patterns were observed below T_c when a laser beam of wavelength 514 nm was incident on the (011) and (111) faces. An illustration of the diffraction patterns appearing on a wall 2.5 m from the crystal is shown in Fig. 10.

The condition of interference of light is

$$n\lambda = d[\sin(i) + \sin(r)], \quad (7)$$

where n is an integer, λ is the wavelength of laser light, d is the distance between domain walls, i is the angle of incidence on a crystal face, and r is the angle the refracted beam makes with the domain walls. Using Eq. (7), for the condition of laser light incident on the (011) face and from the measurement of the diffraction pattern on a wall, d calculated to be approximately $1.5 \mu\text{m}$. The presence of a regular diffraction pattern implies that the domains have remarkable regularity of size. Domain boundaries always formed parallel to the a axis and were directly observed with a polarizing microscope to have dimensions that ranged from 1.0 to $3.0 \mu\text{m}$.

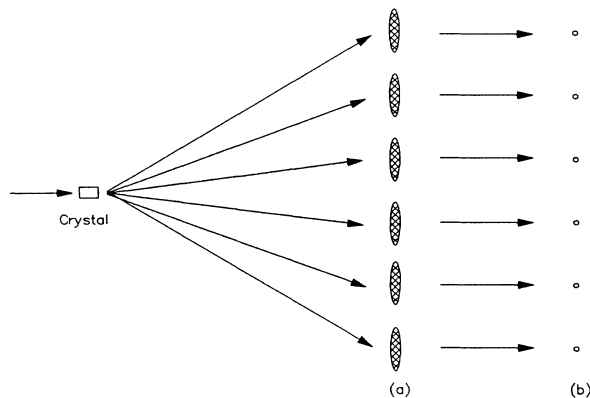


FIG. 10. Laser diffraction from the phenothiazine crystal at (a) room temperature and (b) below T_c .

The spacings of the diffracted light beams do not change with temperature within the 220–295 K range. The size of the diffracted spot (see Fig. 10) varies significantly with temperature, but decreases in size as the temperature is lowered. This is indicative of the degree of increasing translational order with decreasing temperature. This supports the conjecture by van de Waal and Feil of polysynthetic twinning in the room-temperature lattice.

The effect on the monochromatic light scattered from a crystal with a mosaic of domains is to broaden the band shape and reduce the intensity.^{31–33} Thus, as the number of translationally inequivalent lattices increases within a scattering volume, the intensity of the inelastically scattered light decreases. Twinning and domain formation limit the extent of long-range ordering, effectively reducing the size of the lattice the light would sample. This is particularly clear in the spectrum of the [100] V_h Brillouin transverse T_1 component, which significantly decreases in intensity as domain walls became visible (see Fig. 5).

The low intensity of the longitudinal [100] Brillouin component at room temperature suggests that the twinning is present well above the phase-transition temperature. This is consistent with x-ray results that show the atomic displacement parameters for phenothiazine are largest along the c axis of the crystal. This also supports the possibility of polysynthetic twinning with domain walls perpendicular to this axis.

A similar reduction in intensity can also occur through an overdamped lattice vibration. An optical mode of high amplitude was reported in the NMR experiment of Sircar, Mishra, and Gupta where the lattice motion was observed to dampen significantly as the temperature was reduced. In Fig. 5 it can be seen that the transverse T_1 Brillouin component [010] H_h increases significantly in intensity as the temperature is reduced. It is not yet clear if this acoustic mode is coupled to the overdamped optical mode. It is likely that both effects, domain disorder and the high amplitude motion, are linked, and an experiment which exploits the uniaxial nature of the disorder would provide a great deal of information.

B. The acoustic modes and the SPT

Lattice symmetry has a direct effect on Brillouin-scattering tensors and phonon velocities. Table III displays the symmetrically equivalent phonon modes in an orthorhombic lattice. In this experiment the velocities of phonons are consistent with an orthorhombic lattice except for one set. The velocities of the two modes which relate to the stiffness of the e_5 shear strain differ significantly: 348.0 m/sec (within 7° of the true wave vector) versus 1133.0 m/sec (true). These two modes are obviously not symmetrically related unless there is a significant amount of spatial dispersion in the former mode. The lattice, therefore, does not display all the orthorhombic symmetry operations as a result of uniaxial disorder or the lattice is actually disordered monoclinic (quasiorthorhombic). The agreement between the experi-

TABLE III. Summary of experimental acoustic-phonon velocities from various studies. Symmetrically equivalent phonon modes designated by letter (orthorhombic lattice only).

\hat{q}	\hat{e}	Criado (Ref. 9) km/s	This work km/s	Ecolivet <i>et al.</i> (Ref. 6) km/s
[100]	[100]	3.44	3.10	2.44
<i>d</i> [100]	[010]	2.04	1.73	1.97
<i>e</i> [100]	[001]	1.11	1.13	0.430
[010]	[010]	2.36	2.12	2.56
<i>d</i> [010]	[100]	1.54	1.52	1.36
<i>f</i> [010]	[001]	0.789	0.780	1.97
[001]	[001]	1.25	1.64	3.41
<i>e</i> [001]	[100]	0.433	0.619	0.430
<i>f</i> [001]	[010]	0.382	0.348	1.36

mental velocities obtained in this work and those calculated by Criado⁹ for a monoclinic lattice are shown in Table III. The velocities estimated from Ecolivet's *et al.*⁶ set of elastic constants are listed for comparison.

Although the Brillouin spectra in our study exhibited significant dynamic behavior, including polarization breakthrough and multiplet formation from domains, the frequencies of the acoustic modes displayed no anomalous temperature dependence. No softening was observed for any acoustic mode. The frequencies of the two acoustic modes $\{\hat{q}=[100], \hat{e}=[001]\}$ or $\{\hat{q}=[001], \hat{e}=[100]\}$ (equivalent in an orthorhombic lattice) should have decreased to zero frequency at T_c to be consistent with the ultrasound results of Nakayama, Ishii, and Sawada.³

C. Elastic constants

The room-temperature elastic constants in Table IV determined by various investigators and experiments are

shown for comparison. Those listed for Criado⁹ were calculated from velocities extracted from his published dispersion curves based on his lattice-dynamical calculations.

There are significant differences for values of the C_{33} elastic constant which describes the stiffness along the c axis; $C_{33}[C_{33}=C_{cc}]$ is the largest for Nakayama, Ishii, and Sawada³ and Ecolivet *et al.*⁶ and the smallest for this work and those determined from the calculated phonon velocities of Criado.⁹ Confusion in axial labeling of the lattice is not possible because all investigators refer to the x axis as being parallel to the long axis of the phenothiazine molecule. It is possible, however, that molecular or other unit-cell axes were not otherwise correctly determined. The use of twinned specimens also would cause assignment errors.

The morphological differences between a melt-grown and a vapor-grown crystal of phenothiazine are substantial so that a comparison cannot be made between the two. It is generally accepted that melt-grown crystals have higher defect concentrations than vapor-grown samples. Defects in crystals tend to make them harder, and therefore, melt-grown samples are less compressible than vapor-grown samples. Strains generated by the melt-growth process may obscure a spontaneously generated strain or they might appear as a strain instability unrelated to the SPT, e.g., annealing effects. In addition, a large dispersion near $\hat{q}=0$ may exist. Rb_2ZnCl_4 , for example, displays a significant dispersion between the ultrasound and Brillouin measurements of the C_{33} elastic constant.^{34,35}

The nearly complete disagreement with the Brillouin-scattering study of Ecolivet *et al.*⁶ is more problematic. They appear to have used vapor-grown crystals and sampled a large number of \hat{q} vectors, but the inconsistency of their C_{33} value with respect to the macroscopically ob-

TABLE IV. Comparison of elastic constants in kbars from various studies of phenothiazine.

	Nakayama, Ishii, and Sawada (Ref. 3)	Ecolivet <i>et al.</i> (Ref. 6)	Criado (Ref. 9)	This work	This work	This work	This work
Space group	Ortho.	Ortho.	Monoclinic $\beta=92.6$	Ortho.	Monoclinic $\beta=92.6$	Monoclinic $\beta=105.67$	Monoclinic $\beta=110.87$
Method	Ultrasound	Brillouin	Calculated	Brillouin	Brillouin	Brillouin	Brillouin
Elastic constants							
C_{11}		80.9	159.0	128.0	125.0	98.7	92.2
C_{12}		59.7		43.8	43.5	33.0	30.5
C_{13}		2.61		0.126	11.8	-11.3	-0.959
C_{15}					13.8	36.6	36.6
C_{22}		88.7	75.5	60.8	60.8	60.8	60.8
C_{23}		44.6		-34.5	-17.7	-8.86	-5.52
C_{25}					5.34	23.3	24.9
C_{33}		157.6	21.2	33.0	21.2	1.91	2.53
C_{35}	150.0				14.7	-1.60	4.75
C_{44}		25.2	3.90	7.23	6.84	6.91	6.91
C_{46}					-1.88	2.15	2.21
C_{55}		2.50	3.54	2.96	13.4	31.8	33.3
C_{66}	2.0	52.8	40.9	28.9	28.3	28.5	28.5

servable [001] cleavage suggests a misassignment of the crystallographic axis with respect to the crystal habit. Further, they were not able to account for crystal optics in the light-scattering experiments and they give no indication of an awareness of twinned samples. It is not possible to reassign their axes to redetermine elastic constant values from their data because the direct observation of high-symmetry, acoustic modes was not reported. Results based almost entirely on quasitransverse or quasi-longitudinal modes admit an extremely large number of propagation directions and obviate a unique solution.

Ecolivet *et al.*⁶ have assumed that the largest elastic constant of phenothiazine should be along the longest molecular axis based on problematical isostructural arguments from previous elastic constant studies of the polyacenes, anthracene, and naphthalene. The molecular long axis is also the c axis in these acene crystals, but the unit cell of phenothiazine is not in any way isostructural with anthracene or naphthalene. In anthracene and naphthalene, the molecules directly abut one another along the long axis of the molecules. This is not so with phenothiazine; layers of molecules in successive $(00n)$ planes do not pack immediately over one another with abutting ends in a face-centered fashion thereby leaving an intermolecular gap of one unit-cell length perpendicular to the c axis. If phenothiazine were to be compressed along the c axis, the molecules could more easily slip past each other, encountering less interference in this direction. Also, the phenothiazine molecule itself is expected to be more conformationally labile than anthracene and naphthalene, since it may bend in a butterfly fashion along the N - S axis. This would further increase compressibility of the crystal along the c axis.

D. Temperature dependence of elastic constants

Acoustic-phonon measurements and the subsequent determination of unstable strains may be significantly affected as the crystal delaminates into $(00n)$ platelets with changes in temperature and pressure. Strains generated through delamination or by a changing structure may be undiscernable. Further, significant differences in inherent strain of the crystal due to intermolecular interaction and strains generated by the crystal-growth process (i.e., differences in defect concentration) may exist because the single crystals of phenothiazine are highly compliant. The observed hysteretic behavior of the low-temperature domains of phenothiazine may be due to higher-order strain effects such as ferroelasticity.

It is apparent from Figs. 5 through 8 that the elastic stiffness of the phenothiazine single crystal undergoes significant but complex changes through the phase transition. Instabilities in the elastic constants C_{55} and C_{33} have been implicated in the phase transition. The former is associated with a shear in the ac plane and $C_{55} \rightarrow 0$ as $T \rightarrow T_c$ would correspond directly to a transition from $P2_1/c(C_{2h})$ to $Pnma(D_{2h})$. In this work, C_{55} displayed no significant change through the phase transition if the room-temperature lattice is considered to be orthorhombic. The remaining elastic constants, C_{44} and C_{66} , that could be associated with a change in lattice symmetry,

displayed only slight changes determined for any of the four lattice types.

A summary of the behavior exhibited by the complete set of elastic constants obtained in this study suggests an elastic fluctuation near T_c but no significant, symmetry-breaking, structural instabilities. Among the compressional elastic constants, C_{11} and C_{22} show the greatest fluctuation through T_c for both lattice structures. As the temperature is lowered, there appears to be an expansion along the b axis and a compression along the a axis as indicated by C_{22} and C_{11} , respectively. Below T_c , both tend to increase as the temperature is decreased, as would be expected for a contracting lattice. The elastic constant C_{33} remains essentially constant throughout the temperature range for both structures.

Of the off-diagonal compressional elements, only C_{12} exhibits any temperature dependence near T_c . C_{13} displays a significant change but only if the lattice is considered to be monoclinic ($\beta = 105.67^\circ$). C_{23} remains constant throughout the range, but the signs are different in the orthorhombic and monoclinic structures. Of the rest of the elastic constants, the most significant changes occur in the off-diagonal C_{15} element and the more dominant changes in C_{25} and C_{35} only occur if the elastic constants are calculated for monoclinic lattice. Finally, C_{46} , which connects a bc shear under the action of an ab shear (or vice versa), does change slightly through the phase transition, but the most significant change for C_{46} arises from the lattice choice.

It should be noted that of the temperature-dependent elastic constants only the orthorhombic set yields a positive energy density throughout the entire temperature range. This is significant because the orthorhombic lattice has been determined to be the least stable of the three possible structures associated with phenothiazine— $Pnma(D_{2h})$, $P2_1/c(C_{2h})$, or $P2_1(C_s)$ —based on lattice energy calculations.⁹ A negative energy density does not signify an unrealistic result, since phenothiazine forms domains to achieve stability.³⁶ A negative energy density may also imply a metastable phase of the crystal phase above T_c and a trend toward stability at low temperature.

E. Ferroelasticity and the SPT of phenothiazine

A proper, ferroelastic, phase transition is unlikely, since the e_5 strain is apparently not the primary order parameter. An unstable $\hat{q} \sim 0$ acoustic motion is not the principal driving force behind the phase transition in phenothiazine unless the transition is antiferroic. If the phase transition of phenothiazine occurs as disordered monoclinic $P2_1/c(C_{2h})$ to monoclinic $P2_1(C_s)$, the unit cell would be halved and the Brillouin zone of the low-temperature phase would be doubled. In this case, the order parameter would be expected to correspond to an acoustic motion at the Brillouin-zone boundary of the high-temperature phase and the low-temperature monoclinic structure of phenothiazine would not contain a center of inversion. The observation of the pyroelectric effect in this work and by Wood, McCale, and Williams¹¹ supports a $P2_1(C_s)$ low-temperature structure which is

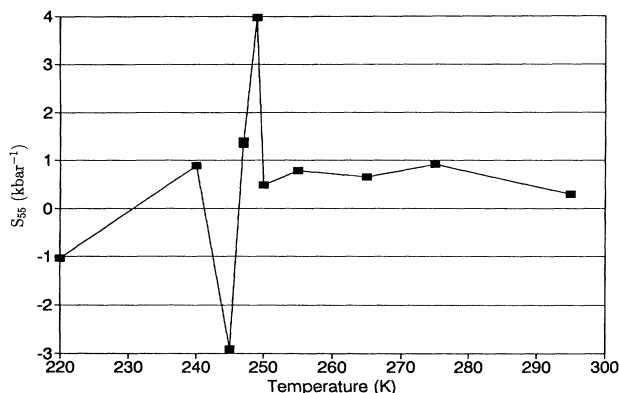


FIG. 11. Temperature dependence of the s_{35} compliance element.

more stable than the $P2_1/c(C_{2h})$ lattice based on lattice static calculations.³⁷ Thus, the phase transition may be antiferroic.

To date, no evidence of cell doubling has been recorded for phenothiazine below T_c . Nevertheless, this does not preclude the possibility because anomalous diffraction effects may be introduced by polysynthetic twinning, disorder or domain formation.

The Raman-active lattice modes of phenothiazine have been observed to show significant anomalies under both changes in temperature and pressure. Thus the possibility of an improper ferroelastic SPT cannot be ruled out and the importance of the unstable optical modes to the SPT in phenothiazine requires further study.

F. Ferrobielasticity

Another explanation may be advanced, however. Phenothiazine may be ferrobielastic. The s_{35} element of the compressibility tensor displays a significant temperature dependence through the phase transition. This is important, since it could make a ferrobielastic crystal appear ferroelastic at low temperature due to an induced e_5 strain. In phenothiazine, the macroscopically observed domains appear to change under a - or b -axis uniaxial stresses. An induced e_5 strain could be generated along with other purely compressional strains if the compressibility coefficient s_{35} induces different responses in twins. Domain switching would then be observed. The temperature-dependent values of s_{35} , determined for $\beta=105.67^\circ$, are displayed in Fig. 11. It is evident that this element shows an anomaly through the phase transition. Thus, a ferrobielastic response of phenothiazine would explain the pressure sensitive domain behavior observed by Nakayama *et al.*¹ and the lack of temperature-dependent behavior of the C_{55} elastic constant found in this study.

VI. CONCLUSION

The specific identity of the lattice structure and the nature of the structural phase transition in phenothiazine have historically generated conflicting conclusions. The single crystals exhibit a number of complicating features which make evaluation of lattice vibrations difficult: uniaxial disorder, macroscopic and polysynthetic twinning, structural domains, structural hysteresis, a strong cleavage plane, and plasticity. These features are a direct manifestation of the complex dynamic behavior of the crystal and this study integrates them into a coherent picture of the anharmonicity of the $\hat{q} \sim 0$ acoustic modes in relation to the phase transition.

The results presented here are consistent with a uniaxially disordered crystal which undergoes an order-disorder phase transition. Structural domains are found to be present above and below T_c ; however, room-temperature domain boundaries are blurred by uniaxial disorder.¹³ As samples of phenothiazine are cooled below T_c , domain walls become visible and cause the multiplet formation observed in the Brillouin spectra. Although it has been postulated that the phase transition of phenothiazine is from disordered $P2_1/c(C_{2h})$ to ordered $P2_1/n(C_{2h})$ (Ref. 13) or from $Pnma(D_{2h})$ to $P2_1/n(C_{2h})$, this research suggests that the actual structural change is from disordered $Pnma(D_{2h})$ [or *disordered* $P2_1/c(C_{2h})$] to ordered $P2_1(C_s)$ (Ref. 14) if the observation of the pyroelectric effect at low temperature is correct. This assignment is based on the behavior of the elastic constants and the observation of a weak pyroelectric effect below T_c .

Inconsistencies in previous studies with the macroscopic properties and a possible misassignment of lattice axes bring the previously conjectured ferroelastic assignment into doubt. Reports of mode softening in the ultrasound experiment on melt-grown samples could arise from annealing effects, crystal delamination and domain formation. The observed domain switching within phenothiazine is probably due to the s_{35} compliance rather than the e_5 strain.

The examination of both the high symmetry and quasi-longitudinal or quasitransverse acoustic modes in this study show that phenothiazine exhibits a higher-order effect such as ferrobielasticity below T_c . Instabilities in elements of the elastic or compliance tensor, rather than the strains, may still play a primary role in the phase transition. NMR studies have strongly supported a phase transition governed by an unstable optical mode or an optical mode which is strongly coupled to the lattice.^{8,15} In addition, recent lattice-dynamical calculations indicate an important role for acoustic-optical mode coupling in the phase transition.³⁸ It is, therefore, possible that the elastic or compliance elements that are unstable through the phase transition and that are of the appropriate symmetry are coupled to the observed anharmonic optical modes.

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