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Reply to "Comment on 'Brillouin-scattering study of the elastic constants of phenothiazine through the phase transition'"

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Disagreement in the ordering of relative magnitudes of the elastic constants of phenothiazine with those of Ecolivet *et al.* is resolved. Dubious methodologies and assumptions employed by Ecolivet *et al.* in their measurements, approximations, and arguments [C. Ecolivet *et al.*, Phys. Rev. B **44**, 5185 (1991)] are noted. Samples employed by these investigators in both their ultrasonic and Brillouin measurements are shown to exhibit properties consistent with impure samples and inconsistent with those of Sartwell and Eckhardt.

Several issues are raised by this Comment. They appear to fall into two categories: (1) a general disagreement with the values reported for the elastic constants of phenothiazine and (2) a disagreement with the relative magnitude of the values for the diagonal elements of constants.

Commercially obtained phenothiazine is quite impure and the method of growth, while quite important, is less critical than the purity of the material. After finding that zone refining and sublimation were inadequate in providing sufficiently pure material, we resorted to chromatographic methods for initial purification followed by multiple sublimations and subsequent zone refining (over 200 passes) in the dark under nitrogen. The resulting material was then used for vapor growth, again in the dark, of crystals using Karl sublimators.¹ Crystals were only removed from inert atmosphere and exposed to light when they were selected and mounted for Brillouin measurements. It is well known that the presence of impurities, even when quite dilute, can easily change the physical characteristics of a solid, especially a molecular one. In particular, the distribution and properties of the defects can be greatly altered by impurities with concomitant alteration of the elasticity. Ecolivet *et al.* do not note having taken such extensive steps as we in the purification of their phenothiazine.

Observation of the striae was only possible by examination using a microscope. Visual observation is insufficient for their detection. Lack of experimental information by Ecolivet *et al.* does not admit knowing whether their failure to observe striae arises from lack of microscopic examination or from actual absence from the crystals.

An exact relation for the mutual compensation of the refractive index variation and density variation can only be obtained for cubic crystals.² The expression is of doubtful use for highly anisotropic systems such as monoclinic/orthorhombic phenothiazine where both the tensors for thermal expansion and the optical indicatrix are of low symmetry. The fact that color is observable for the crystal indicates the presence of near ultraviolet resonances in reasonable proximity to the exciting frequency of the laser. Even at frequencies reasonably far

removed, resonances can strongly affect the behavior and asymmetry of the optical indicatrix for anisotropic lattices. The polarization of the transitions and their vibronic structure, which usually exhibit significant dependence on temperature, lead to important variances in the values of the refractive index as a function of direction. It is because of this that direct measurement of the temperature and directional dependence of the refractive index was sought in our experiment rather than assuming the refractive index behavior would be independent of both of these parameters. That a single value of the refractive index is valid for all directions of an anisotropic crystal such as phenothiazine, we have shown to be quite unlikely by direct measurement. These direct measurements also strongly indicate influence of a nearby resonance. And that the optical indicatrix should have the same asymmetry and thermal response as the thermal expansion tensor thereby yielding compensation seems rather improbable to us.

The agreement of the various measurements of Ecolivet *et al.* and their collaborators is unsurprising since they apparently used the same samples. There is a paucity of experimental details in the original paper, although some are now available in their comment, but it is not clear how they set the velocities of their acoustic modes in the Brillouin experiment. Our calibration was with ultrapure benzene which has a very well characterized phonon velocity; the calibration was repeated for each scattering experiment or adjustment of the interferometer. Had the ultrasound results been used by Ecolivet *et al.* to set the velocities for the Brillouin measurements, additional agreement would have been imposed for these two determinations.

Because of the difficulty with the crystallographic determinations by the various crystallographers themselves, we had determined our crystals' crystallographic parameters using x-ray precession methods. We have redetermined the lattice constants using a four circle automated diffractometer with special provision for determination and assignment of crystal faces. The parameters found are those given in the literature. However, in the space group assignment used in precession measure-

ments for the Brillouin study, we chose $Pbmn$ (unprimed system) and did err in failing to permute the axes to the $Pmna$ (primed) setting (i.e., $a \rightarrow c'$, $b \rightarrow a'$, and $c \rightarrow b'$). Both space groups define the same lattice; they arise only from different axial labelings. Ours was chosen because an easy identification with the synthetically twinned monoclinic lattice was sought. The permutation of axes puts the relative ordering of the magnitudes of the elastic constants in agreement with those of Ecolivet *et al.* Since it is only a question of labeling, the reported elastic constant magnitudes are unchanged. The axes drawn in Fig. 2 are for $Pbmn$ and the face assignments are correct. The text should have stated that the domain boundaries are perpendicular to the b axis as shown in Fig. 2.

Our reference to cleavage was simply meant to reinforce the fact that intermolecular forces, necessarily related to the elastic behavior, in the c -axis direction must be small for such cleavage to occur. A direct measurement would be to exert a linear stress along the c axis and observe its effect. This was done in the course of a piezomodulated Raman spectroscopy study on phenothiazine where it was reported that small stresses caused ready delamination of planes perpendicular to the c axis.³ Delamination was not observed for uniaxial stresses along either the a or b axes of the crystal. Such experiments are performed with quite small stresses and we suggest that they are not *unreasonably* related to the behavior of the solid in the elastic regime. It should be emphasized that the separation was not associated with the striae depicted in Fig. 2 of the original paper.

Care must be taken in comparisons of organic crystals. Aside from being crystals, there is no real commonality between an organic crystal such as phenothiazine and a metal. The variance of behavior of organic crystals is such that to compare crystals of molecules of such different chemical and physical properties as phenothiazine and polyphenyls is questionable. In terms of its separation under stress, the phenothiazine is best compared to graphite or 1,4-diphenyl-1,3-butadiene. Both are aromatic, organic crystals which delaminate in a similar fashion

to phenothiazine; polyphenyls and metals do not delaminate.

Ferrobielasticity was presented as a possible higher-order effect which might have reconciled the disparate experimental results and which would be consistent with what is presently known of phenothiazine.² The later piezomodulation spectroscopy study offers further support for the suggestion. We are surprised that a suggestion of another possibility that might be considered to rationalize the available data would warrant comment. It is certainly not the major point of the study. It was *consistent with data currently available* and suggestive of further work that, as Ecolivet *et al.* point out, would have to be done to validate the hypothesis.

While the disagreement on the ordering of the magnitudes of the constants can be resolved, their values are nevertheless in notable disagreement. Examination of the data at hand suggests that the preparation of the phenothiazine, particularly in the purification procedures, may have led to quite different materials. It is well known that highly purified organic crystals are often quite fragile, plastic, and prone to dislocation formation. These behaviors were so evident with our crystals that comment was made in our report. That no mention of such behavior was made by Ecolivet *et al.* suggests that their samples possessed quite different physical behavior, even on the macroscopic scale, than did ours. In fact, we found extreme difference in the macroscopic physical behavior of our melt-grown crystals from that of the vapor grown. Regardless of extensive measures to prevent reaction, melt-grown samples could not be obtained with the same degree of purity as the vapor grown ones. The melt-grown crystals were much harder and did not delaminate and would appear to have properties more like those of Ecolivet *et al.* Those investigators comment on the great similarity of their melt and vapor grown crystals. Albeit a too commonly used reason, the sample preparation and different purities of phenothiazine is strongly indicated as a major cause of the disagreement in the measured values of the two groups.

¹N. Karl, in *Crystals, Growth, Properties and Applications*, edited by H. C. Freyhardt (Springer-Verlag, Berlin, 1980), Vol. 4, p. 1.

²A. Mierzejewski and C. Ecolivet, *J. Phys. C* **15**, 4695 (1982).

³J. Sartwell and C. J. Eckhardt, *Phys. Rev. B* **48**, 13 361 (1993).