
COMMENTS

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Comment on “Brillouin-scattering study of the elastic constants of phenothiazine through the phase transition”

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In the paper of Sartwell and Eckhardt (denoted as SE) [Phys. Rev. B **48**, 12 438 (1993)] controversial results about ferroelasticity of phenothiazine are presented. These authors cast some doubts on the validity of our measurements [Ecolivet *et al.*, Phys. Rev. B **44**, 4185 (1991)]. We detail here the method we used and its advantages and we point out some questionable results and assertions of the former paper. In particular, we present a comparison of the diagonal elastic constants of phenothiazine obtained from different techniques, which have been ignored or misused in the SE paper. The results here, rather, show a convergence against the results of the SE paper. Finally, the problem of the quality of the crystals is addressed.

First of all we would like to insist on some points in our paper¹ which seem to have been misunderstood or misinterpreted. The crystals used in our study were vapor grown and of very good optical quality. They were absolutely free of striae at room temperature and presented only domains at low temperatures where they have been detected by Brillouin scattering. As stated in the text, Brillouin scattering was mostly performed in back-scattering on natural faces, the only crystal optics correction was performed when the sample was rotated in order to find the photon wave vector inside the crystal. In the other geometry the parallel faces of the sample are at 45° of the incident and scattered beams so that the internal scattering angle depends on the refractive index which finally cancels in the Brillouin shift formula provided that the incident and scattered beams have the same polarization. With these geometries we have been able to observe six modes along crystallographic directions and these modes are either true longitudinal or true transverse modes but true transverse modes can also be found in the main crystallographic planes when they are polarized perpendicular to these planes so that as many as 24 true modes velocities have been measured on a total of 72. Moreover the derived elastic constants are confirmed by ultrasonic measurements² which of course may produce some strains on those fragile samples, but the agreement between our sets of elastic constants is reasonable.

We would also like to point out a peculiarity of the elastic constants determination by Brillouin scattering

when it involves the refractive index in the shift formula. We have shown³ that there is a mutual compensation of the density variation by the refractive index variation, which is also due to density variation, since

$$C_{ii}(T) = \rho(T) V^2(T) \propto \frac{\rho(T)}{n^2(T)} \nu^2(T), \quad (1)$$

where $\nu(T)$ is the Brillouin shift, ρ the volumic mass, V the sound velocity, and n the refractive index. A polynomial approximation of Eq. (1) assuming a Lorentz-Lorenz law for the refractive index variations gives, when $n = 1.65$, a complete compensation at first order in ΔT whereas the second-order coefficient is as small as the square of the volume thermal expansion coefficient which rarely exceeds 10^{-3} K^{-1} . We have reported $C_{33}(T)$ in Ref. 1 measured with $n_a = 1.60$, in that case the first-order coefficient of the error is about 8×10^{-2} times the volume thermal expansion coefficient, so that even with a high value of this coefficient (10^{-3} K^{-1}) density and refractive index variations should not induce errors larger than 10^{-2} Gpa ($C_{33} = 15.7 \text{ Gpa}$). Of course we may admit that the Lorentz-Lorenz law is not exact in that kind of crystals but the error will be at least one order of magnitude below the 15 to 35 % relative errors estimated by Sartwell and Eckhardt. In order to obtain a better accuracy with a measured $n(T)$ one should have $\Delta n \leq 2 \times 10^{-3}$ with a density variation perfectly known. In the same kind of way, it is surprising to see in their Table I refractive index variations as large as 0.07 (a 4%

TABLE I. Diagonal elastic constants of phenothiazine previously determined by ultrasonics (Ref. 2), Brillouin scattering (Ref. 1), and lattice dynamics calculations (Refs. 4 and 5) compared to the ones obtained by Brillouin scattering in the paper of Sartwell and Eckhardt.

Gpa	Ultrasonics (Ref. 2)	Brillouin (Ref. 1)	Lattice dynamics (Refs. 4 and 5)	SE
C_{11}	8.3	8.09	16.2	12.8
C_{22}	7.5	8.87	16.1	6.1
C_{33}	15	15.76	25.4	2.1
C_{44}	2.2	2.52	1.9	0.68
C_{55}	0.2	0.25	2.9	1.34
C_{66}	6.6	5.28	6.0	2.83

variation) in one kelvin, even near the phase transition. It looks more reasonable to assign it in a large part to an experimental error, but here the magnitude of the error is not reported.

In order to reconcile our results we may think of a mistake in axis labeling but it turns out that this paper is rather confusing about this. First, low-temperature domain boundaries are said to be perpendicular to the a direction (p. 12 441 and p. 12 444) but in Fig. 2 they seem perpendicular to the b axis. Besides, on p. 12 445 it is stated that "all investigators refer to the x axis as being parallel to the long axis" but we never use such notation since we called this direction c . Moreover the authors use the lattice dynamics work of Criado⁴ in order to support their results but they likely made a mistake in axis labeling probably because Criado used a relaxed $Pnma$ structure $b > a > c$ instead of $c > b > a$ in $P2_1/n$, resulting in wrong arguments about the anisotropy of elastic constants. Diagonal elastic constants obtained by ultrasonics,² our results by Brillouin scattering,¹ lattice dynamics results,^{4,5} and Brillouin results of the SE paper are collected in Table I in order to properly compare missing ultrasonics data, correct lattice dynamics values, and the last Brillouin scattering results. This table underlines the reasonable agreement between our results and ultrasonics as well as a similar anisotropy of compression elastic constants obtained by lattice dynamics, although the absolute values are by a factor of 2 with experiment results. However lattice dynamics cannot in itself be a proof for

experimental results but rather a test on the ability to modelize the crystalline field. Nevertheless there is obviously an order of magnitude between the C_{33} value of Sartwell and Eckhardt and all the other ones.

In the SE paper, these authors also compare elastic constants with the cleavage properties of phenothiazine saying that the elastic constant related to the longitudinal mode "perpendicular to the cleavage plane, C_{33} , should be significantly smaller than those within the plane, C_{22} and C_{11} ." This argument seems unreasonable since it relates the stress over strain ratio for the zero stress limit, which defines elasticity, to the maximum stress state, at fracture where strains are no longer linear with a considerable influence of plastic deformations leading to the fracture. In the field of molecular crystals many counterexamples against this argument can be found, polyphenyls are only a few of them⁶ and for metals it is well known that it is easier to break a steel needle than an iron one although the steel modulus is much larger.

However it is also possible that their measurements could have been perturbed by the room temperature microdomains they have detected. In particular they estimate the thickness of these domains in the μm range but it is also the range of the phonon wavelength they investigate and in that case the scattering volume is far from being infinite at the phonon scale. It is also possible that these domain walls may slow down or even stop the order parameter relaxation which according to our study occurs in the 0.1 ns range near the phase transition and then the softening of C_{55} may be quenched. On the contrary, the softening of C_{55} has been observed as well on melt grown as on vapor growth crystals by ultrasonics (unpublished data).

Moreover we are also quite skeptical about the relevance of their Fig. 11 for the demonstration of ferrobielasticity when anomalies are obtained from only one temperature point on each side of a broken line and only 11 temperatures were studied for a phase transition, which is rather few when some effects need proof. In addition, previous theoretical investigations of ferrobielasticity⁷ did not retain its possibility in orthorhombic crystals.

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