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# STUDY OF THE ELASTIC STIFFNESS CONSTANTS OF THIOUREA BY BRILLOUIN SCATTERING

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All the elastic stiffness constants of thiourea have been measured at room temperature. The value of $C_{66}$ ($0.7 \times 10^{10}$ dynes/cm$^2$) is very low. The $C_{11}$ and $C_{33}$ constants exhibit discontinuities at 169 and 202 K. The longitudinal acoustic phonons propagating in the c direction are very strongly damped in the vicinity of 202 K.

THIOUREA is an orthorhombic crystal; the point group symmetry is $D_{2h}$ above 202 K and $C_{2v}$ below 169 K.[1] It is well known that four phase transitions appear at 169, 176, 180 and 202 K. Among the five phases (called I, II, III, IV, V in order of increasing temperatures) two of them (I, III) are ferroelectric and a superlattice structure appears in the II, III, IV phases.[2] Although many studies on the dielectric [1,3] and thermal properties of this material have been performed, the data concerning its elastic properties are still lacking. Only the temperature dependence of one elastic stiffness constant has been measured by ultrasonic way.[4]

We report here on our experimental results obtained by Brillouin scattering, with a Fabry–Perot interferometer of resolving power 200 000 and an He–Ne 50 mW laser ($\lambda = 6328$ Å). The reference axes used are $OX_1$, $X_2$, $X_3$ parallel to the **a**, **b**, **c** edges of the elementary cell. At room temperature $a = 7.655$, $b = 8.537$ and $c = 5.520$ Å.[5] The principal refractive indices are $n_a = 1.634$, $n_b = 1.806$, $n_c = 1.789$ [7] and the density is $\rho = 1.406$ g/cm$^3$.[3]

When the Brillouin scattering at 90° by longitudinal acoustic phonons propagating along the **a**, **b**, **c** direction is studied, the relations between the frequency shifts of the Brillouin lines and the elastic stiffness constants $C_{ii}$ are very simple, since the velocity of the low frequency acoustic phonons is $V = (C_{ii}/\rho)^{1/2}$. Table 1 gives the results obtained at 20°C.

Two measurements can be made of $C_{11}$, $C_{22}$ and $C_{33}$ and we estimate the accuracy on these constants to be about 1%.

The formulae used for the measurement of the other elastic stiffness constants are more complicated. However, results previously obtained allow their determination with an accuracy somewhat lower. We found ($10^{10}$ dyn/cm$^2$):

$C_{12} = 2.4 \mp 0.4$ $\quad C_{13} = 7.2 \mp 0.4$ $\quad C_{23} = 5 \mp 0.4$

$C_{44} = 2 \mp 0.1$ $\quad C_{55} = 5.7 \mp 0.1$ $\quad C_{66} = 0.7 \mp 0.3$

The $C_{66}$ value is extremely low and the lack of precision prevented us to study the temperature dependence of this constant. Among all the other elastic stiffness constants, $C_{11}$, $C_{22}$ and $C_{33}$ exhibit the strongest temperature dependence.

The $C_{22}$ constant (Fig. 1) has a monotonous variation vs temperature and the slope of the curve shows a discontinuity only at 169 K.

The results obtained for $C_{11}$ (Fig. 2) are in agreement with the ultrasonic measurements:[4] there are two discontinuities at 169 K and especially at 202 K. Around 202 K there is an enlargement of the Brillouin line, but we do not find the same phenomena at 169 K,

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*Table 1. Results of the measurement of the longitudinal elastic stiffness constants at* 20°C

| Incident light | Scattered light | Frequency shift of the Vv component ($10^{-3}$ cm$^{-1}$) | $\rho V^2 \times 10^{-10}$ dyn/cm$^2$ | Elastic stiffness constant $10^{10}$ dyn/cm$^2$ |
|---|---|---|---|---|
| $[\bar{1}10]$ | [110] | 359 | 10,22 | $C_{11} = 10{,}25$ |
| $[\bar{1}01]$ | [101] | 364 | 10,28 | |
| $[1\bar{1}0]$ | [110] | 567 | 25,42 | $C_{22} = 25{,}37$ |
| $[0\bar{1}1]$ | [011] | 516 | 25,32 | |
| $[10\bar{1}]$ | [101] | 439 | 14,95 | $C_{33} = 14{,}86$ |
| $[01\bar{1}]$ | [011] | 394 | 14,77 | |

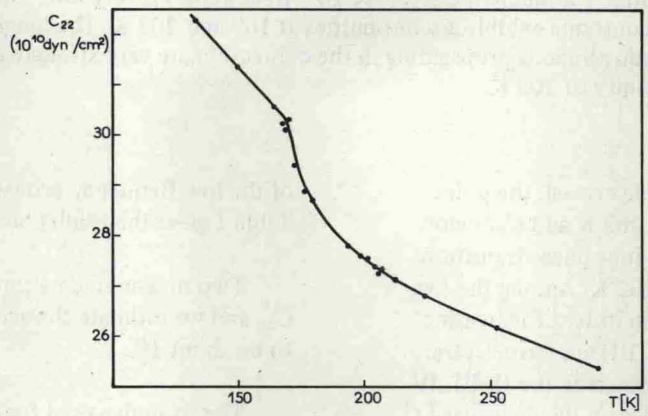



Fig. 1. Temperature dependence of $C_{22}$.

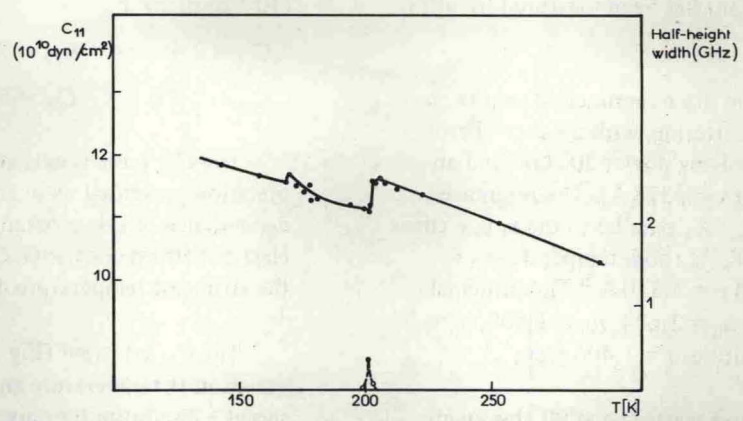



Fig. 2. —— Temperature dependence of $C_{11}$. ----- Half-height width of the deconvoluated Brillouin line.

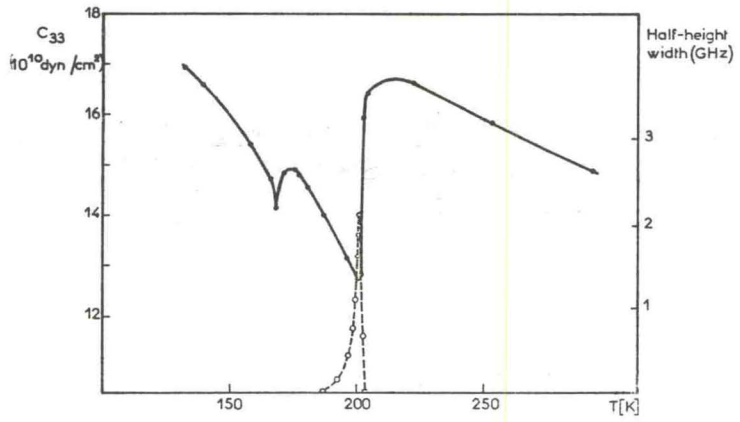



Fig. 3.—— Temperature dependence of $C_{33}$. ------ Half-height width of the deconvoluated Brillouin line.

although there is an ultrasonic attenuation at this temperature.

The $C_{33}$ constant (Fig. 3) shows strong discontinuities at 169 K and 202 K. As for $C_{11}$, there is a strong enlargement of the Brillouin line around 202 K, mainly in phase IV. The half-height width is proportional to log $(T-202)/202$. The same observation was made for the absorption coefficient of the ultrasonic wave propagating in the **a** direction.[4]

The properties, around 202 K, of the longitudinal acoustic phonons propagating in the **a**, **b**, **c** directions must be compared to the results of the study of the modulated structure which appears in phase IV.[6] The thiourea molecules are subjected to displacements composed, around 202 K, of a translation parallel to **c** and a very weak rotation around an axis parallel to **b**. The damping of the longitudinal acoustic phonons is correlated to the amplitude of the static displacements of the molecules at 202 K.

Finally, we did not observe any anomaly of the elastic stiffness constants at the 176 and 180 K transition points.

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Toutes les constantes élastiques de la thiourée ont été mesurées à température ordinaire. La valeur de $C_{66}$ ($0.7 \times 10^{10}$ dynes/cm$^2$) est très faible. Les constantes $C_{11}$ et $C_{33}$ manifestent des discontinuités à 169 et 202 K. Les phonons acoustiques longitudinaux qui se propagent dans la direction **c** sont très fortement amortis au voisinage de 202 K.