ELASTIC CONSTANTS OF CRYSTALS FROM LIGHT SCATTERING MEASUREMENTS*

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1. Introduction

According to the theory of Einstein which was later elaborated by Leon Brillouin, the scattering of light in a material medium is ascribed to the coherent reflection of light waves by the periodic stratifications produced by the elastic (sound) waves of thermal origin assumed to be present and traversing the medium in all directions. One of the important consequences of Brillouin's theory (1922) is that the moving elastic waves would give rise to spectral shifts of frequency in the diffused light which are in the nature of a Doppler effect. The simple equation derived by Brillouin for the change of frequency is the following:—

$$\frac{\Delta\nu}{\nu} = \pm \frac{2v_e}{c} n \sin \frac{\theta}{2} \tag{1}$$

where

$\Delta\nu$ = is the frequency shift of the scattered light.

ν = the frequency of the incident light wave.

v_e = velocity of the elastic waves giving rise to scattering.

c = velocity of light.

n = refractive index of the medium.

θ = angle of scattering.

Several investigators have considered the theory of the thermal scattering of light in crystals as proposed by Brillouin and came to the conclusion that in a crystal only three pairs of Doppler components occur in the scattered light due respectively to the three types of elastic waves which are propagated with different velocities in any given direction in the crystal. The symmetry of the crystal was not taken into consideration and the influence of birefringence on the Brillouin components was neglected. However, Chandrasekharan (1950, 1951) has shown recently that the birefringence of the crystal when taken into account leads to the remarkable result that there are in general not three but twelve Doppler components which can appear

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in the case of a birefringent crystal. The most general expression for the birefringence of the crystal is given by

$$\frac{\Delta\nu}{\nu} = \pm \frac{v_e}{c} \sqrt{n_i^2 + n_s^2 - 2n_i n_s \cos\theta}, \qquad (2)$$

where n_i and n_s are the two refractive indices of the crystal for the directions of incidence and scattering. Since n_i and n_s can each take two values, there should be four pairs of values for (n_i, n_s) in equation (2). Further, for a given direction of elastic wave normal there are three types of elastic waves, each of which has a different velocity v_e. Thus from equation (2) it is easily seen that there are 12 possible values for $\Delta\nu$. In the case of a cubic crystal, the general equation (2) reduces to equation (1).

Although the existence of Doppler components in the light scattered by crystals was predicted by the theory of Brillouin as early as 1922, an experimental confirmation of the same was not forthcoming till much later. This is essentially due to the difficulties that beset an experimental observation of such low frequency shifts in the light diffused by crystals. In most of the crystals the frequency shifts of the Doppler components is of the order of ·5 to 3 cm.$^{-1}$ and consequently it is imperative to employ some high resolving power instrument to separate these. Besides, it is not often possible to procure large transparent crystals free from inclusions and the parasitic illumination which arise from these leads to the presence of the unmodified radiation along with the Brillouin components. Nevertheless, the fine structure of the scattered radiation predicted by theory was first observed by Gross (1930) in quartz and later by Raman and Venkateswaran (1938) in gypsum and L. Sibaiya (1938) in Rochelle salt. More recently the utilisation of the λ 2537 radiations of a quartz mercury arc in conjunction with a three metre quartz spectrograph by R. S. Krishnan (1947) and by Krishnan and Chandrasekharan (1950, 1951) has made possible an unambiguous recording and observation of these Brillouin components in quartz, diamond, alumina and a few other crystals and the existence of these in the light diffused by crystals may now be taken to be a well established fact.

It is now possible for us to make such an accurate study of the frequency shift, intensity and polarisation of these Doppler components that we will proceed to examine in detail the implications of the theory of thermal scattering of light in crystals. From equations (1) and (2) one finds that the frequency shifts $\Delta\nu$ of the scattered light are directly related to the elastic wave velocities. By a precise measurement of the frequency shifts of the Doppler components for different orientations of the crystal one can calculate

the acoustic velocities for different directions. From a knowledge of the effective wave vectors and using Christoffel's equation, one can now readily evaluate the elastic constants. Thus the thermal scattering of light in crystals and solids affords a new method for the determination of elastic constants.

2. Experimental Method

From what was said earlier, it will be evident that use of the visible radiations of the mercury arc makes it essential to employ large specimens free from incursions, etc., in order to record the genuine scattered radiation. This is particularly important since in most crystals, irregularities of a permanent nature like dislocations, etc., lead invariably to a certain amount of unmodified radiation in the nature of Tyndall scattering and this tends to a masking of the Brillouin components that are closeby. It is not always possible to have crystals which are free from such defects and satisfy the needs of the experiment. But these difficulties are easily obviated by the use of the resonance radiation of mercury for exciting the Brillouin components since the unmodified radiation can easily be eliminated from the scattered radiation by the use of a mercury vapour filter. Further as the intensity is proportional to λ^{-4} and n^8 the enormously increased scattering power in the ultraviolet is of added advantage and shortens the exposures necessary for recording the spectra. Over and above these advantages, the separation of the Brillouin components increases with the frequency of the incident radiation. The use of the resonance radiation therefore combined with Hilger three metre quartz spectrograph which has a dispersion of about 14 cm.$^{-1}$ in the λ 2537 region is adequate to make accurate measurements of the frequency shifts and to evaluate the elastic constants.

Using this technique, various crystals have been investigated in our laboratory and the results obtained therefrom are given in the next section.

3. Results and Discussion

In Plate X are reproduced the Brillouin spectra recorded with some typical crystals. In general it is found that except in the case of diamond the calcite, the transverse components are relatively weak in conformity with the theoretical calculations (V. Chandrasekharan, 1952, 1953). A quantitative verification of the directional variation of the acoustic wave velocity has been carried out so far only in the case of diamond and quartz. In Plate XI are reproduced the enlarged photographs of the spectra taken for four different orientations of a specimen of quartz with reference to the directions of incidence and observation. The first letter on the right-hand side of each photograph represents the direction of incidence while the

TABLE I

Cubic Crystals

No.	Crystal	Light incident along	Light scattered along	Angle of scattering in degrees	Direction of Elastic wave-normal	Nature of Brillouin components	Shift observed in cm.$^{-1}$	Effective elastic constant		
								Theoretical expression	Value calculated from observed shifts $\times 10^{-11}$ dynes/cm.^{2}	Value calculated from known elastic constants $\times 10^{-11}$ dynes/cm.^{2}
1	LiF	[100]	[010]	90	[1$\bar{1}$0]	Longitudinal	1·83	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	12·55	12·43
2	NaCl	[100]	[010]	90	[1$\bar{1}$0]	Longitudinal	1·44	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	4·80	4·31
3	KCl	[100]	[010]	90	[1$\bar{1}$0]	Longitudinal	1·21	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	3·34	2·93
4	Diamond	[111]	[$\bar{1}\bar{1}\bar{1}$]	180	[111]	Transverse	7·0	$\frac{1}{3}(c_{11}+c_{12}+c_{44})$	36	33
		[111]	[01$\bar{1}$]	90	$\approx$ [4$\bar{1}$,10]	Longitudinal	8·7	..	112	105
		[111]	[01$\bar{1}$]	90	$\approx$ [4$\bar{1}$,10]	Transverse	5·59	..	46	38·7
		[2$\bar{1}\bar{1}$]	[111]	90	$\approx$ [$\bar{1}$44]	Longitudinal	8·56	..	108	110·9
		[2$\bar{1}\bar{1}$]	[111]	90	$\approx$ [$\bar{1}$44]	Transverse	5·63	..	47	41·7
		[2$\bar{1}\bar{1}$]	[$\bar{1}\bar{1}\bar{1}$]	90	$\approx$ [811]	Longitudinal	8·09	..	97	97·1
		[2$\bar{1}\bar{1}$]	[$\bar{1}\bar{1}\bar{1}$]	90	$\approx$ [811]	Transverse	5·88	..	51	42·6
		[2$\bar{1}\bar{1}$]	[01$\bar{1}$]	90	$\approx$ [3$\bar{4}$1]	Longitudinal	8·50	..	107	111
		[2$\bar{1}\bar{1}$]	[01$\bar{1}$]	90	$\approx$ [3$\bar{4}$1]	Transverse	5·58	..	36	37·3

TABLE II

Birefringent Crystals

No.	Crystal	Light incident along	Light scattered along	Angle of scattering in degrees	Direction of elastic wave-normal	Nature of Brillouin components	Shift observed in $cm.^{-1}$	Effective elastic constant		
								Theoretical expression	Value calculated from observed shifts $\times 10^{-11}$ dynes/$cm.^2$	Value calculated from known elastic constants $\times 10^{-11}$ dynes/$cm.^2$
1	α-Quartz	$[0\bar{1}0]$	[001]	90	[011]	Longitudinal	1·90	..	10·80	9·83
	,,	[010]	[001]	90	$[01\bar{1}]$	Longitudinal	2·07	..	12·82	12·91
	,,	[100]	[001]	90	[101]	Longitudinal	1·96	..	11·23	11·69
	,,	[100]	[010]	90	[110]	Longitudinal	1·75	..	9·16	9·02
	,,	[100]	$[\bar{1}00]$	180	[100]	Longitudinal	2·36	c_{11}	8·33	8·54
	,,	[010]	$[0\bar{1}0]$	180	[010]	Longitudinal	2·22	$\frac{1}{2}(c_{11}+c_{44})$ $+\sqrt{\frac{1}{4}(c_{11}-c_{44})^2+c_{14}^2}$	7·37	9·32
	;,	[001]	$[00\bar{1}]$	180	[001]	Longitudinal	2·51	c_{33}	9·42	10·57
2	Calcite	[011]	$[0\bar{1}\bar{1}]$	180	[011]	Longitudinal	3·18	..	12·71	13·76
	,,	[011]	$[0\bar{1}\bar{1}]$	180	[011]	Longitudinal	2·89	..	12·22	13·76
	,,	[011]	$[0\bar{1}\bar{1}]$	180	[011]	Transverse	1·15	..	1·66	2·58
	,,	[011]	$[0\bar{1}\bar{1}]$	180	[011]	Transverse	1·41	..	2·90	2·58
3	Alumina	..	..	90	[001]	Longitudinal	2·45	c_{33}	21·4	56·3
4	Barite	[110]	$[1\bar{1}0]$	90	[100]	Longitudinal	1·55	c_{11}	10·84	8·83
	,,	[110]	$[\bar{1}10]$	90	[010]	Longitudinal	1·47	c_{22}	9·74	7·81
	,,	[001]	$[00\bar{1}]$	180	[001]	Longitudinal	2·13	c_{33}	10·23	10·38

second stands for the direction of observation (Fig. *a*) in Plate XI is the mercury spectrum heavily exposed in order to record the unabsorbed part of λ 2536·5 and its wings. In this picture, λ 2534·8 appears very broad due to overexposure. In accordance with the theoretical predictions, we notice a marked variation of $\Delta\nu$ with the orientation of the crystal with reference to the directions of incidence and scattering.

The measured values of the frequency shift of the Brillouin components observed in the case of four cubic crystals and four birefringent crystals are entered in Tables I and II. The directions of incidence, scattering and elastic wave normal with reference to the crystallographic axes of the specimens have also been given in the same tables. Using formulæ (1) and (2) given earlier, the values of the effective elastic constants have been calculated in all these cases and given in the last column (9) of Tables I and II. The last column of the same tables contains the corresponding values calculated from the known elastic constants using the theoretical expression given in Column 8. In some cases the theoretical expressions for the effective elastic constants are not given as they are very complicated. A critical study of Tables I and II reveals a fairly good agreement between the values of the effective elastic constants calculated from the observed Brillouin shifts and the corresponding values calculated from the elastic constants determined in the usual way. The only serious discrepancy noticed in the tables is in the case of alumina. This is due to the fact that the width of each component was nearly three-fourth of the observed shift (Krishnan, 1947). In all probability the observed width is due to the overlapping of the longitudinal and transverse components.

From an analysis of the results given above it is evident that accurate measurements of the shifts of Doppler components appearing in light scattered by crystals afford a new method for the determination of the elastic constants. Employing proper experimental technique, with specifically chosen directions of incidence and observation in the crystal and utilising in addition the polarisation characteristics of the different species, it is possible to separate unambiguously the Brillouin components due to the different acoustic waves and thereby investigate the complete elastic behaviour of crystals. In view of the sharp nature of the Brillouin components the accuracy attainable in the determination of the elastic constants by such light scattering studies is high.

4. SUMMARY

Details of the methods of evaluating the elastic constants of any crystal from the observed frequency shifts of the Brillouin components arising from

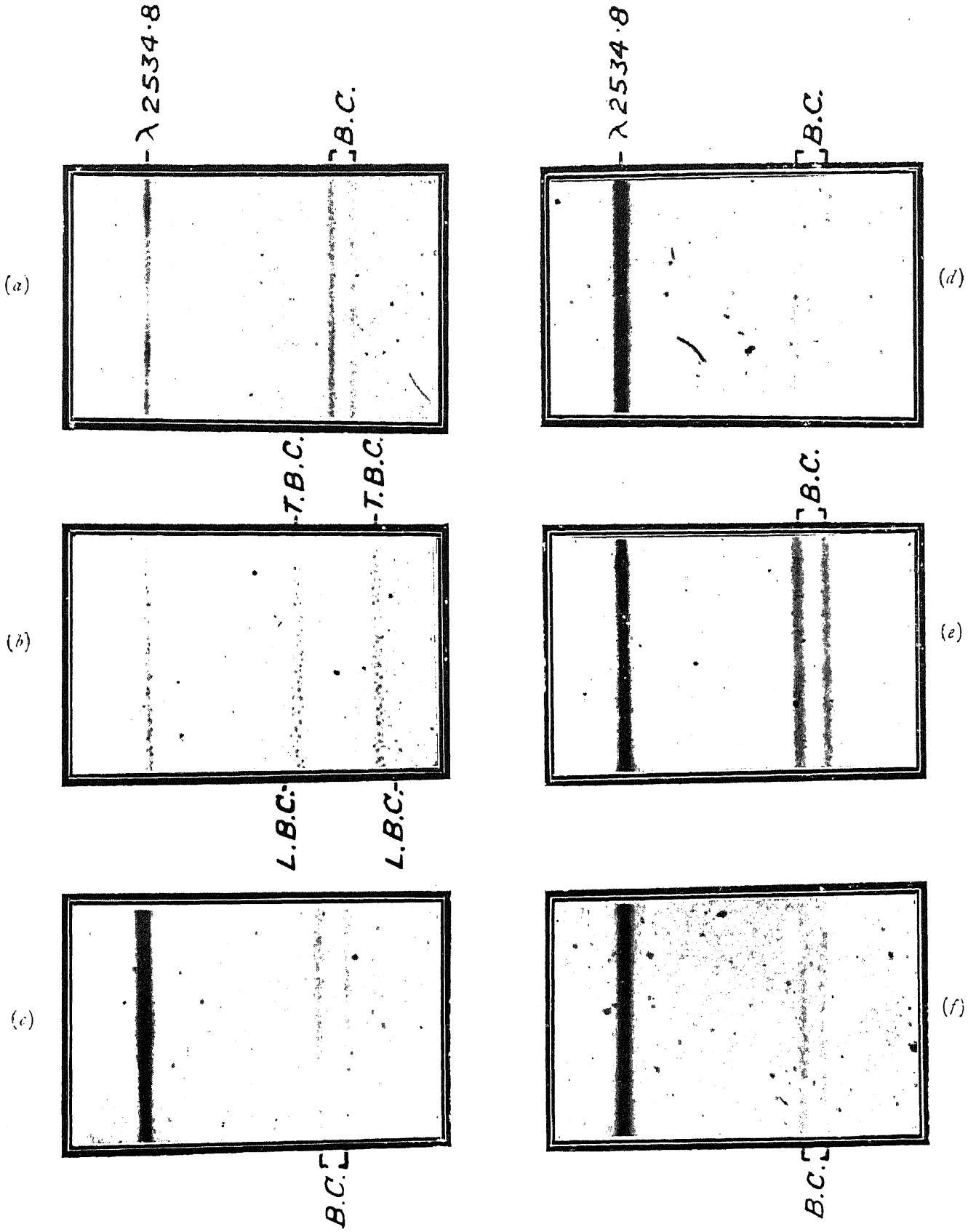

FIG. 1. The Brillouin spectra of crystals under ultra-violet excitation.

(*a*) Rock salt (*b*) Diamond (*c*) Barite
(*d*) Calcite (*e*) Quartz (*f*) Gypsum

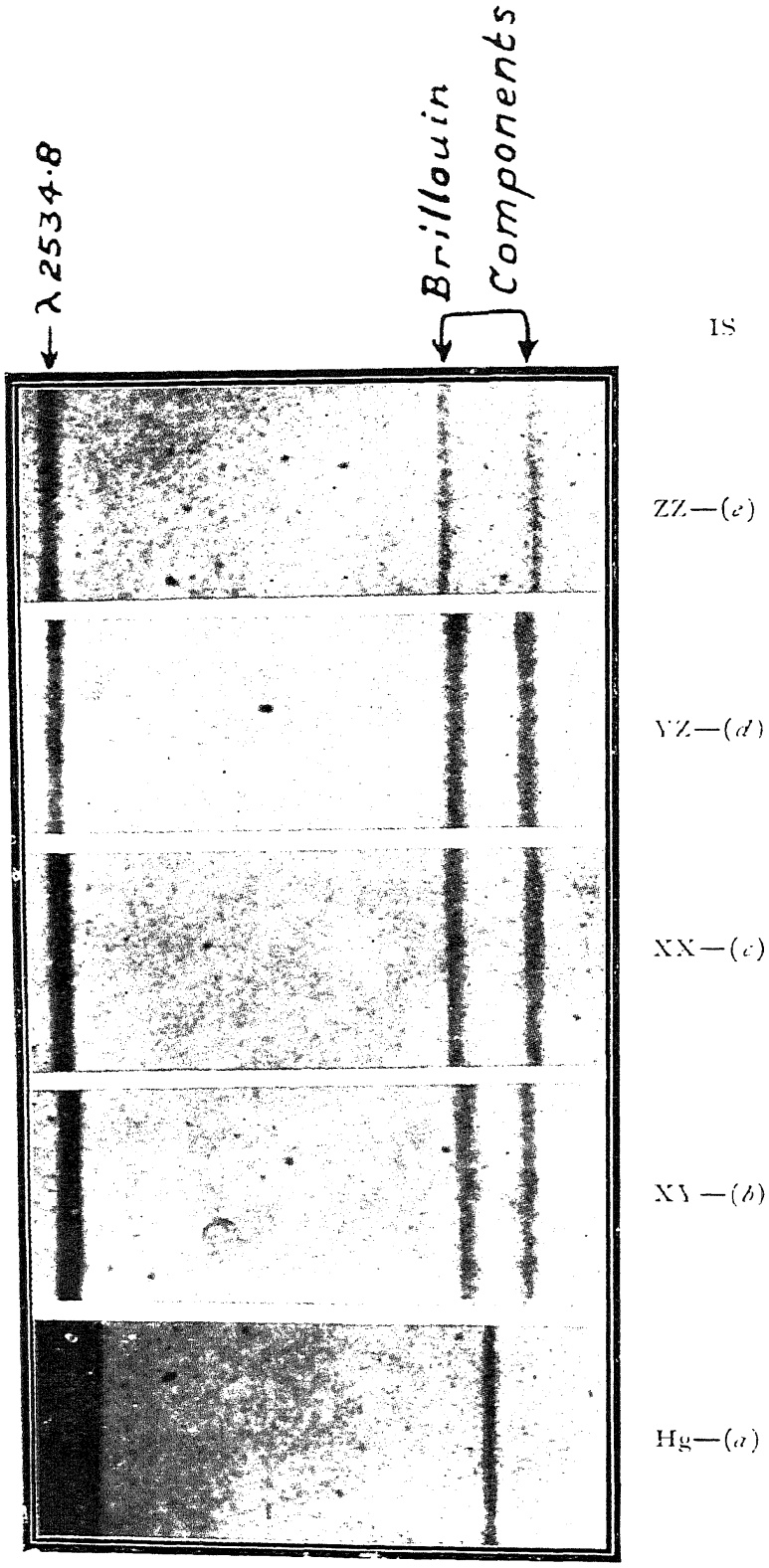

FIG. 2. (a). Heavily exposed mercury spectrum.
(b), (c), (d) & (e). Scattered spectrum of Quartz for four different orientations.

the thermal scattering of light have been indicated. From the measurements of the frequency shifts of the Brillouin components recorded using ultraviolet excitation in the case of four cubic crystals and four birefringent crystals, the effective elastic constants have been evaluated and have been compared with the values calculated using the elastic constants determined by other methods. The agreement is found to be very satisfactory. Thus light scattering in crystals affords yet another method of determining the elastic constants.

5. References

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