THERMAL SCATTERING OF LIGHT IN CRYSTALS

Part II. Diamond

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1. Introduction

As is well known, Brillouin (1922) put forward the view that a crystalline medium might be regarded as a continuum and that the diffusion of light by it arises from the coherent "reflection" of the light waves by sound waves of thermal origin traversing it in all directions. Consequently, the scattered spectrum should reveal Doppler-shifted components with frequency shifts from that of the incident monochromatic light of frequency ν, being given by

$$\Delta\nu = \pm 2\nu \frac{v}{c}\mu \sin\frac{\theta}{2}, \tag{1}$$

where v is the velocity of sound in the medium, μ its refractive index, c the velocity of light in vacuum and θ the angle of scattering. As there are one longitudinal or compressional and two transverse or equivoluminal waves in any particular direction travelling with different velocities, one might expect under favourable conditions to get six Brillouin components in the light scattered by any crystal. In Part I of the series (R. S. Krishnan and V. Chandrasekharan, 1950), the investigations on the fine structure of the thermal scattering of light in quartz using the λ 2536·5 mercury resonance radiation and a three-metre quartz spectrograph in combination with a mercury vapour filter to absorb the unmodified radiation from the scattered light, have been reported. The scattered spectrum in the case of quartz exhibits only one pair of Brillouin components due to the longitudinal sound waves in the medium. The dependence of the frequency shifts on the orientation of the crystal with reference to the directions of incidence and of scattering has been quantitatively verified for seven different settings of the crystal.

In the case of diamond, on account of the exceptionally large velocity of sound waves in it and its high refractive index, the Doppler-shifted components have been recorded by R. S. Krishnan (1947) using a medium quartz

spectrograph. With the help of the larger E1 spectrograph, two pairs of Brillouin components have been recorded by him, the outer arising from the longitudinal sound waves in diamond and the inner brighter ones due to the transverse sound waves. It was considered desirable to re-investigate the case of diamond using the three-metre quartz spectrograph. This has been carried out by the author for four different orientations of the diamond with reference to the directions of incidence and of observation.

2. Experimental Details

The two specimens of diamond, kindly lent by Sir C. V. Raman and used in the present investigation were the same as those studied by R. S. Krishnan. One of them, namely, NC 60, was in the form of a rectangular plate ($10 \times 6 \times 1 \cdot 3$ mm.) with faces and edges well polished. The length, breadth and thickness of the diamond were respectively parallel to $[01\bar{1}]$, [111] and $[\bar{2}11]$. The specimen was well suited for studying the effect of orientation. However, as it was slightly yellowish in colour, its transparency to $\lambda 2536 \cdot 5$ radiation was not great. The other specimen NC 174 had curved edges and therefore, was not well suited for the study.

Diamond NC 60 was held in a special brass holder with one of its faces vertical and facing a vertical water-cooled quartz mercury arc of special design. The light scattered in the transverse horizontal direction and emerging out of another face was focussed on the slit of a Hilger three-metre spectrograph. It had a dispersion of $14 \cdot 1$ cm.$^{-1}$ per millimetre in the $\lambda 2536 \cdot 5$ region. Because of its large dispersion and the high resolving power of 300,000, the displaced components were recorded so well separated from one another that the shifts could be estimated even with a glass scale.

The light scattered by a crystal is generally accompanied by parasitic light both due to flaws in the specimen as well as from reflections from its surface, especially so in the case of small specimens. Hence a filter of mercury vapour kept in the path of the scattered light suppressed the unmodified resonance radiation from the scattered light and thus enabled the Brillouin components to be recorded on a clear background. Because of the effective water-cooling, magnet control and continuous evacuation, the arc emitted the resonance radiation ($\lambda 2536 \cdot 5$) with great intensity. Even so, exposures of the order of two days had to be given to record both pairs of Brillouin components clearly, using a slit-width of $0 \cdot 02$ mm.

With the help of a medium quartz spectrograph, the Brillouin components arising from the transverse waves were recorded for backward scattering along [111]. However, due to the small depth of illumination, the

backwardly scattered light was very feeble and even with exposures of the order of five days, the recorded spectrum was too faint to be reproduced.

3. Results

A typical photograph showing the Brillouin components and the first order Raman spectrum is reproduced in Fig. 1 (*a*) (same size). It is seen that the parasitic light is reduced to a minimum *so that* λ 2534·8 *Hg line is recorded with an intensity less than that of the Brillouin components due to the transverse waves*, while the λ 2576·3 Hg line is not recorded. The absorption of the mercury vapour kept in the scattered path extends to a certain degree on either side of λ 2536·5, the absorption being greater on the longer wavelength side. However, in the case of diamond, on account of the large separation of even the Brillouin components due to transverse waves, the mercury vapour produces practically no asymmetry or reduction in intensity of the Brillouin components.

Figs. 1 (*d*), (*e*) and (*f*) in Plate (XIX) show the Brillouin components in transverse scattering for three different settings of diamond (enlarged 20 times in each case). They show clearly the dependence of the separation of the components on orientation. Fig. 1 (*b*) is an enlargement of the Doppler-shifted components in quartz for backward scattering, while Fig. 1 (*c*) shows the components both in quartz as well as in diamond for transverse scattering (photographed on the same plate). The Brillouin components in diamond are definitely broader than those in quartz. This is probably due to the large convergence of the incident light necessitated by the small dimensions of the crystal. The semi-angle of convergence amounts to at least 15° in the case of diamond. This could not be reduced further without undue increase in the time of exposure.

The frequency shifts of the Brillouin components for five different orientations studied have been measured, assuming that the separation between λ 2534·76 and λ 2536·52 is equal to 27·02 cm.$^{-1}$ (Burns, 1950) and entered in Table I along with the corresponding values of the shifts calculated using equation (1) and the known elastic constants. The values of the various constants used are $\mu = 2{\cdot}624$, $\rho = 3{\cdot}514$ gm. cm.$^{-2}$, $\nu = 39{,}412$ cm.$^{-1}$, $c_{11} = 95 \times 10^{11}$, $c_{12} = 39 \times 10^{11}$ and $c_{44} = 43 \times 10^{11}$ dynes/cm.^{2} (Bhagavantam and Bhimasenachar, 1946). The agreement between calculated and observed shifts is not very satisfactory. Both Krishnan's and the author's values are definitely higher than those calculated for the components due to transverse waves, while the author's measurements show a slightly smaller value for the longitudinal component.

In cases 1 and 2, the direction of incidence with reference to the orientation of the crystal was kept the same, while the light scattered transversely in opposite directions was recorded. The observed shifts of the Brillouin components are different for the two cases. This difference arises from the fact that the direction of the elastic wave responsible for light scattering is different in the two cases. Only, if either the direction of incidence or of observation coincides with either a two-fold or four-fold symmetry axis of the crystal or if there is a plane of reflection perpendicular to either, will the two cases be identical. The wave-normal of the elastic waves responsible for light scattering travels along the external bisector of the incident and scattered directions and hence, in case 1, it was approximately along [$\bar{1}$44] or about 10° from the [011] direction, while in case 2, it was along [811] or about 10° from the [100] direction. The separation of the longitudinal components from the transverse components is smaller in case 2 [Fig. 1 (*e*)] than in case 1 [Fig. 1 (*f*)]. In cases 3 and 4, as the direction of the scattered light [011] is one of two-fold symmetry, these differences are absent. Hence the six possible settings of a parallelopiped with reference to the directions of incidence and observation reduce to only four for the diamond used. In case 4, as the light had to be incident along the breadth through one edge and the scattered light was taken out through another edge, the recorded spectrogram was too weak to be reproduced.

Along any given direction, there are three possible sound velocities. However, in most cases, the sound velocities for the two sets of transverse waves are nearly the same for diamond. The maximum difference is along the dodecahedral axis, the corresponding calculated separation of the Brillouin components arising from the two sets of transverse waves being 5·4 and 4·35 cm.$^{-1}$ Hence, in this case, two pairs of transverse components should have been separately recorded or if they are not seen clearly resolved, the observed transverse components should at least appear very broad. Case 1 in which the effective wave travels along a direction inclined only 10° to [011], corresponds nearly to the above case. But only one pair of Doppler components of normal width due to transverse waves was recorded. This is indeed surprising.

4. Intensity Measurements

By microphotometering the negatives and using the standard method of graded intensity marks, an estimate of the intensities of the longitudinal and transverse Brillouin components and of the 1332 cm.$^{-1}$ Raman line was made for the first three cases of Table I. The ratio of intensities of the transverse to the longitudinal Brillouin components is entered in the last

TABLE I*

No.	Fig. No.	Incident al ong	Scattered along	Scattering angle	Nature of Brillouin components	Shift observed in cm.$^{-1}$ Author's values	Krishnan's values in cm.$^{-1}$	Shift calculated cm.$^{-1}$	Ratio of intensities T.B.C./L.B.C.	Ratio of intensities Raman/B.C.
1	*f* & *a*	[2$\bar{1}$1]	[111]	90°	Longitudinal	8·56	..	8·66	2·3	12·0
		[2$\bar{1}$1]	[111]	90°	Transverse	5·63	..	5·39 4·38		
2	*e*	[2$\bar{1}$1]	[$\bar{1}\bar{1}$1]	90°	Longitudinal	8·09	8·2	8·11	3·3	8
		[2$\bar{1}$1]	[$\bar{1}\bar{1}$1]	90°	Transverse	5·88	6·7	5·36 5·29		
3	*d* & *c*	[2$\bar{1}$1]	[01$\bar{1}$]	90°	Longitadinal	8·50	9·0	8·68	1·8	7
		[2$\bar{1}$1]	[01$\bar{1}$]	90°	Transverse	5·58	5·5	5·02 4·78		
4		[111]	[01$\bar{1}$]	90°	Longitudinal	..	8·7	8·43	..	..
		[111]	[01$\bar{1}$]	90°	Transverse	5·59	5·6	5·12		
5		[111]	[$\bar{1}\bar{1}$1]	180°	Longitudinal	..	..	12·47	..	..
		]111]	[$\bar{1}\bar{1}$1]	180°	Transverse	7·0	..	6·69		

* T.B.C.=Transverse Brillouin component. L.B.C.=Longitudinal Brillouin component.

but one column of Table I. It is seen that the ratio is always greater than one and that it varies with the orientation of the crystal. The ratio of the intensity of the Raman line to the sum of the intensities of the two pairs of Brillouin components in different cases is entered in the last column of Table I. Unlike in quartz, for which the principal Raman line 466 cm.$^{-1}$ is weaker than the Brillouin components, the Raman line 1332 cm.$^{-1}$ of diamond is nearly seven to twelve times as intense as the sum of the intensities of the Brillouin components at room temperature.

In the estimation of the intensities, no correction has been made for the finite angle of convergence of the incident beam. Further, there were complications arising from the appreciable intensity of reflection of the incident light from the back surface of the crystal as a consequence of its high refractive index. At normal incidence the reflectivity of diamond for λ 2537 amounts to as much as 20%. Its effect has been neglected in the estimation of intensities.

According to Leontowitsch and Mandelstamm (1932), the light reflected or transversely scattered by sound waves of thermal origin in a medium is given by the formula.

$$I=\frac{\pi^2}{2\lambda^4}kT\mu^8\left\{\frac{2(p_{12}^2+p_{44}^2)}{c_{11}+c_{12}+2c_{44}}+\frac{p_{44}^2}{c_{44}}\right\}, \tag{2}$$

where I is the intensity of the light scattered by 1 cm.^{3} of the substance for natural light of unity intensity, λ the wave-length, μ the refractive index, c_{ik} elastic constants, p_{ik} Pockel's elasto-optic constants and T the temperature of the scattering substance.

According to Hans Mueller's analysis (1938), the first term inside the double brackets in (2) is the contribution due to the longitudinal sound waves, while the second term is due to the transverse waves. The values of the elasto-optic constants as determined by Ramachandran (1950) recently are $p_{11}=-0{\cdot}31$, $p_{12}=0{\cdot}09$, $p_{44}=-0{\cdot}12$. Using these corrected values, the intensities of the longitudinal and transverse Brillouin components are respectively $0{\cdot}23\times10^{-5}$ and $0{\cdot}37\times10^{-5}$. Thus the transverse components should be about 1·6 times as bright as the longitudinal components. This behaviour is due to the large value of p_{44} as compared to p_{12} unlike in many other crystals of cubic symmetry in which generally p_{44} is very much smaller than p_{12}. The observed values for the intensity ratio are nearly of the same order of magnitude as predicted by the theory.

However, the theory of Leontowitsch and Mandelstamm is valid only for a specific orientation of a cubic crystal, namely, when the directions of incidence and of observation coincide with the cubic axes. The intensity would be independent of orientation only in amorphous substances, which have spherical symmetry and for which a relation exists between p_{11}, and p_{12} and p_{44}, namely, $p_{11}-p_{12}-2p_{44}=0$ and a similar relation $c_{11}-c_{12}-2c_{44}=0$. In crystals belonging to the cubic class, the above relations are not satisfied and consequently, both the shift and intensity of the Brillouin components should vary with orientation, as is shown by the observed results in the case of diamond. The intensities of thermal scattering in cubic crystals for specific orientations have been worked out by the author and the results will be reported later.

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5. Summary

The thermal scattering of light in diamond has been studied with the help of a three-metre quartz spectrograph using the $\lambda 2536 \cdot 5$ mercury radiation as exciter. The scattered spectrum shows two pairs of Doppler-shifted components clearly resolved from each other, one pair due to the longitudinal sound waves and the other due to the two sets of transverse sound waves which have nearly the same velocity. The dependence of the frequency shifts on the orientation of the crystal with reference to the incident and observation directions has been verified for five settings. The observed shifts are not in very good agreement with the values calculated from the elastic constants, the transverse components having shifts *definitely* larger and the longitudinal components having shifts slightly smaller than the expected values. The interesting fact that the shifts of the Brillouin component are generally different for light scattered transversely in opposite directions, the direction of the incident light being kept the same, has been verified in two cases. The difference arises from the fact that the direction of propagation of the elastic waves responsible for light scattering is not necessarily the same in the two cases. The transverse components are found to be 1·5 to 3 times more intense than the longitudinal components, depending on the orientation of the crystal. The principal Raman line 1332 cm.$^{-1}$ is 7 to 12 times as intense as the sum of the intensities of the two pairs of Brillouin components.

References

1. Bhagavantam, S. and Bhimasenachar, J. .. *Proc. Roy. Soc.*, A, 1946, **187**, 38.
2. Brillouin, L. .. *Ann. de Physique*, 1922, **17**, 88.
3. Burns, Adams and Longwell .. *J. Opt. Soc. Am.*, 1950, **40**, 339.
4. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, A, 1947, **26**, 339.
5. ——— and Chandrasekharan, V. .. *Ibid.*, 1950, **31**, 427.
6. Leontowitsch and Mandelstamm .. *Phy. Z. Sowjet*, 1932, **1**, 317.
7. Mueller, H. .. *Proc. Roy. Soc.*, A, 1938, **166** 425.
8. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, A, 1950, **32** 171.