THERMAL SCATTERING OF LIGHT IN CRYSTALS

Part I. Quartz

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1. INTRODUCTION

THE phenomenon of the scattering of light in crystalline media was first noticed with quartz (R. J. Strutt, 1919). That the observed effect was due to the thermal agitation of the atoms in the crystal was established by C. V. Raman (1922) who showed that the intensity of scattering in a perfectly clear specimen of quartz was in agreement with that calculated using the well-known scattering formula of Einstein and Smoluchowski. This explanation was later confirmed by Landsberg, Mandelstamm and Leontowitsch (1927) who studied the temperature dependence of the intensity of scattering in quartz. While examining the light scattered transversely by liquids with the aid of a high resolving power instrument soon after the discovery of the Raman effect, Gross (1930) reported the existence of a fine structure for the Rayleigh radiation, *i.e.*, an undisplaced central line and two lines on either side with wave-lengths slightly different from that of the incident monochromatic radiation. He claimed to have observed a similar effect with crystalline quartz also. The appearance of the displaced components was first predicted by Brillouin (1922). On the basis of his theory, the observed displacements of frequency are regarded as Doppler effects arising from the reflections of the light wave by the progressive sound waves of thermal origin in the scattering medium. The frequency shifts of the displaced or the Brillouin components are given by the formula

$$\triangle \nu = \pm\, 2\nu\,(v/c)\,\mu \sin \theta/2, \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where v is the velocity of sound in the medium, μ its refractive index, c the velocity of light in vacuum and θ is the angle of scattering. In any given direction in a crystal, there are in general three distinct sets of sound waves, one of them being a longitudinal or compressional wave and the other two being transverse or torsional waves with the vibrations in two mutually perpendicular directions. As these waves travel with different velocities and if conditions are favourable, one might expect to observe six Doppler shifted components in the light scattered by a crystal, That the effect contemplated by Brillouin does arise in crystals is now a well-established experimental fact. In this connection, references may be made to the work of Raman and Venkateswaran (1938) on gypsum, of Sibaiya (1938) on Rochelle salt and of Krishnan (1947) on diamond and alumina. But a detailed study of the phenomenon and its dependence on crystal orientation has so far been done only for diamond, whereas in the other cases, the effect has been recorded for one orientation only. The success achieved with diamond was mainly due to the use by Krishnan of the Rasetti technique for such studies. Even in the case of diamond, for want of a suitably cut plate of diamond of the ultra-violet transparent type, the investigations were incomplete. We have now undertaken a systematic investigation of the fine structure of the Rayleigh radiation and its dependence on crystal orientation in a large number of crystals. Using the ultra-violet excitation and a Hilger three-metre quartz spectrograph, we have successfully recorded the Brillouin components in quartz (crystalline and amorphous), calcite, rock-salt, etc. In this paper the results obtained with crystalline quartz are presented.*

2. Earlier Work on Quartz

Using λ 4358 radiation of mercury and a 30 step echelon spectroscope, Gross (1930) reported to have noticed a doubling of the Rayleigh radiation in quartz. He neither reproduced any photograph nor recorded any measurements. This was explained by him as due to the feebleness of the pattern and also due to the ambiguity arising from the appearance of different orders. In the first report, Gross (1932) mentioned as having observed four displaced components, two of the first order and two of the second order. In a later communication he (Gross, 1938) mentioned the following:—" Recent researches with crystalline quartz warrant the conclusion that the Rayleigh line of quartz appeared to have six modified components, *i.e.*, three components on each side of the undisputed line."

Using the λ 2536·5 mercury resonance radiation and an aluminised Fabry Perot etalon, Krishnan (1945) photographed the Brillouin components due to the longitudinal sound waves in the light scattered backwards in quartz for three different orientations of the crystal. Due to the finite width of the exciting line and the fact that the thickness of the thinnest spacer for the etalon available was 1 mm., the positive and negative components from consecutive orders overlapped. It was, therefore, not possible to make accurate measurements. The observed features of the interference pattern for the different orientations was, however, qualitatively accounted for,

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* A preliminary report has already appeared in *Nature*, 1950, **165**, 406.

3. EXPERIMENTAL TECHNIQUE

Two specimens of quartz were used in the present investigation. One of them had its natural faces well developed, and was 1½″ long. Three mutually perpendicular faces were cut in the crystal. These faces were normal to the three crystallographic axes X, Y and Z respectively. Preliminary observations were made with this specimen. As it was of small size and as it had some inclusions, for quantitative studies a clearer specimen of Brazilian quartz from Sir C. V. Raman's personal collection of minerals was used. The authors are grateful to Sir C. V. Raman for the loan of the specimen. The specimen was worked into a rectangular block of size ($6\cdot5 \times 4\cdot5 \times 3\cdot5$ cm.) with its parallel faces normal to the X, Y and Z axes. All the faces were well polished.

The $\lambda 2536\cdot5$ mercury resonance radiation emitted by a specially designed magnet-controlled water-cooled quartz arc was used as the source of radiation in the present study. For observing the transverse scattering, the rectangular block was placed over the arc with one of the axes parallel to the discharge. In the case of backward scattering, the light from the arc was allowed to fall on the crystal along one of its axes with the aid of a right-angled prism. The scattered light was focussed on the slit of a Hilger three-metre quartz spectrograph. This instrument has a dispersion of 13·8 wave-numbers per mm. in the $\lambda 2536$ region and a resolving power of 300,000. In the case of most crystals, the separation of the Brillouin components for $\lambda 2536\cdot5$ is of the order of ± 2 cm.$^{-1}$ Because of the high dispersion and large resolving power of the three-metre spectrograph, the displaced components in crystals could be recorded with this instrument clearly and well separated from one another.

If the crystal under investigation is completely free from flaws and inclusions and if the optical arrangement is perfect, the scattered light should exhibit only the displaced components and not the incident radiation. The conditions mentioned above are seldom realised in practice and in any particular case the scattered light may be mixed up with parasitic illumination. In the present investigation, therefore, a filter of mercury vapour maintained at room temperature was kept in the path of the scattered light. This filter effectively suppressed the unmodified resonance radiation from the scattered light, thus enabling the Brillouin components to be recorded on a clear background. With effective water-cooling, magnet control and continuous evacuation of the arc, the $\lambda 2536\cdot5$ line was emitted from the arc with an intensity so great as to enable the Brillouin components arising from it to be recorded satisfactorily with an exposure of six hours and a slit width of 0·01 mm.

A typical photograph is reproduced in Fig. 1 (*a*). In this spectrogram the λ 2534·8 Hg line is recorded with the same intensity as the displaced components, while the λ 2576·3 Hg line is scarcely visible.

It is well known that the resonance line is usually accompanied by wings of some sort on either side. The width and intensity of the wings are very much influenced by the conditions of running of the arc (Mitchell and Zemansky, 1934). In order to find out with what intensity the wings were present in the mercury spectrum under the special conditions of running mentioned in the last paragraph, a series of photographs of the spectrum of the direct arc was taken with varying exposures using the mercury filter at room temperature as in the scattering experiments. The photographs are reproduced in Fig. 2. An enlarged print of a moderately exposed spectrum is reproduced in Fig. 1 (*b*). In place of the resonance line, a sharp feeble line appears, being the unabsorbed part of the resonance line on the shorter wavelength side. This line has a width of the order of 0·2 cm.$^{-1}$ and its separation from the centre of λ 2536·5 is 0·55 cm.$^{-1}$ It has an intensity less than 1/30th the intensity of λ 2534·8. When the spectrum is considerably over-exposed, one observes the ghosts accompanying the λ 2534·8 and also faint wings of the resonance line appearing asymmetrically situated on either side of the unabsorbed line of the resonance radiation. See also the microphotometer record reproduced in Fig. 3 (*a*). It is interesting to note that while the ghosts appear as sharp lines,

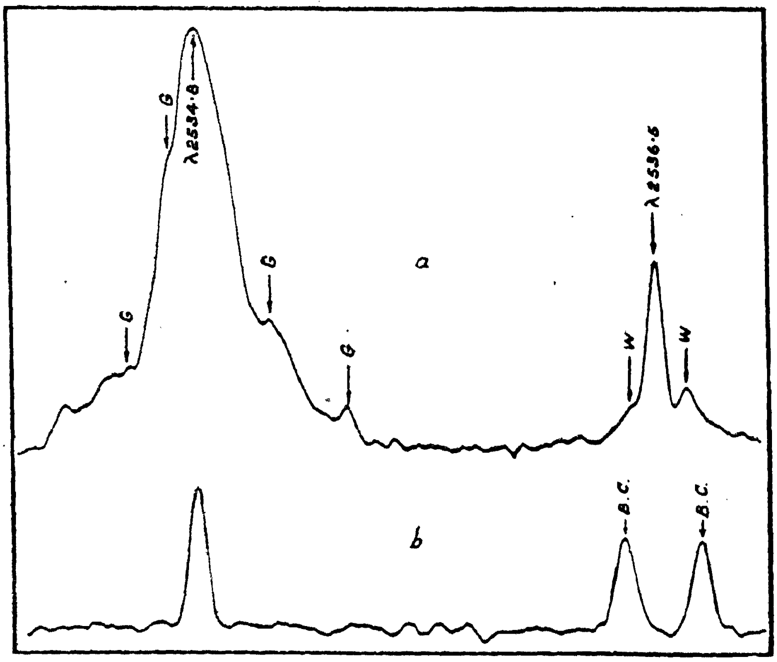

FIG. 3 (*a*) Microphotometer record of a heavily exposed filtered mercury spectrum
G = ghost, W = wing

(*b*) Microphotometer record of the scattered spectrum of quartz showing the Brillouin components, *B.C.*

the faint wings of the resonance radiation are broad and diffuse. Moreover, the edge of either wing adjacent to the resonance radiation is most intense, the intensity gradually falling off as one moves away from the resonance line. This is a very important characteristic which differentiates the so-called wings from the real Brillouin components. By a comparison of Figs. 1 (*a*) and 1 (*b*) in Plate XX, it would be obvious that with the exposures required to record the Brillouin components, neither the unabsorbed part of the resonance line nor its wings appear at all. They do not, therefore, vitiate the results obtained with reasonably good crystals like the specimen of quartz used in the present investigation. See Fig. 3 (*b*).

It is a known fact that the absorption of mercury vapour is not confined to $\lambda 2536 \cdot 5$ but extends though feebly but asymmetrically on either side, the absorption being greater on the longer wavelength side (Mitchell and Zemansky, 1934). Due to this effect, the Brillouin components may also be reduced in intensity to a small extent, but this reduction in intensity is more for the component on the longer wavelength side. The components are not therefore recorded with equal intensity. See Fig. 6 (*b*).

4. RESULTS

Figs. 1 (*a*) and 1 (*b*) in Plate XX, represent two photographs of the spectrum of the scattered light taken with the specimen No. 2, while Fig. 1 (*b*) represents the comparison mercury spectrum taken under identical conditions. While in Fig. 1 (*a*) the mercury line $\lambda 2534 \cdot 8$ is just visible, the two Brillouin components are very clearly seen in the photograph. In the heavily exposed photograph of the scattered spectrum (Fig. 1 *c*) the important Raman line of quartz, *i.e.*, 466 cm.$^{-1}$ is just visible. It has an appreciable width. Unlike in the case of diamond (Krishnan, 1947), the Brillouin components in quartz are about ten times more intense than the principal Raman line.

In order to investigate the dependence of the separation of the Brillouin components on the orientation of the crystal, the spectrograms of the scattered light were photographed for seven different orientations of the crystal, four for transverse scattering and three for backward scattering. In Fig. 4 of Plate XXI, are reproduced the photographs (enlarged twenty times) of the scattered spectra taken for four different orientations of the specimen of quartz with reference to the directions of incidence and observation. The direction of incidence is indicated by the first letter on the right-hand side of each photograph, while the second letter indicates the direction of observation. For example, ZZ represents backward scattering along the Z axis, XY represents transverse scattering in the XY plane, *i.e.*, incident along X axis and scattered along Y axis. Fig. 4 (*a*) is an enlarged photograph of the mercury spectrum which was heavily exposed in order to record the unabsorbed part of λ 2536·5 and its wings. In this picture, the λ 2534·8 is considerably broadened due to overexposure. It is seen that only one pair of Brillouin components arising from the longitudinal sound waves appears in all the photographs, showing thereby that the components due to the transverse waves are of feeble intensity. This is in accordance with the theoretical calculations (Chandrasekharan, 1950). As is to be expected, the shift of the displaced components is different for different orientations. It is maximum for backward scattering along the optic (Z) axis and minimum for transverse scattering in the XY plane. It may be remarked that the components appear broader for the transverse scattering [Figs. 4 (*b*) and 4 (*d*)] than for the backward scattering [Figs. 4 (*c*) and 4 (*e*)]. This is due to the fact that the angle of scattering in the former case was less well defined than that in the latter case.

The frequency shifts of the Brillouin components for the seven different orientations studied have been measured and entered in Table I. The last column contains the corresponding values of the shifts calculated using equation (1) and the known elastic constants of quartz. The agreement between the calculated and observed values is very satisfactory except for backward scattering along Y axis. For this case the difference cannot be accounted for as due to errors of measurement. It is interesting to note that in the YZ plane, the sound velocity along the internal bisector of Y, Z is different from that along the internal bisector of —Y, Z.

TABLE I

Frequency Shift of Brillouin Components in the Light Scattered by Quartz

No.	Incident along	Scattered along	Scattering angle	Shift observed cm.$^{-1}$	Shift calculated cm.$^{-1}$
1	—Y	Z	90°	1·90	1·8
2	Y	Z	90°	2·07	2·07
3	X	Z	90°	1·96	1·97
4	X	Y	90°	1·75	1·73
5	X	X	180°	2·36	2·38
6	Y	Y	180°	2·22	2·49
7	Z	Z	180°	2·51	2·64

5. TEMPERATURE DEPENDENCE

According to the well-known theories, the intensity of the Brillouin components should increase with temperature. In order to verify this result in the case of quartz, the following experiment was carried out. A thin rectangular plate of crystal quartz of size 1″ × 1″ × $\frac{1}{4}$″ with polished faces was used. The specimen was mounted inside a furnace similar to the ones used in this laboratory for Raman effect studies at high temperatures. The furnace was mounted horizontally just above the arc. Two photographs were taken of the scattered light with the crystal maintained at 60° C. and at 375° C. respectively. Using a slit width of 0·025 mm. exposures of the order of 12 hours were given. The enlarged prints are reproduced in Fig. 5 in Plate XXI and the corresponding microphotometer records in Fig. 6. The increase in brightness of the Brillouin components as the temperature is increased is beautifully illustrated by Figs. 5 and 6.

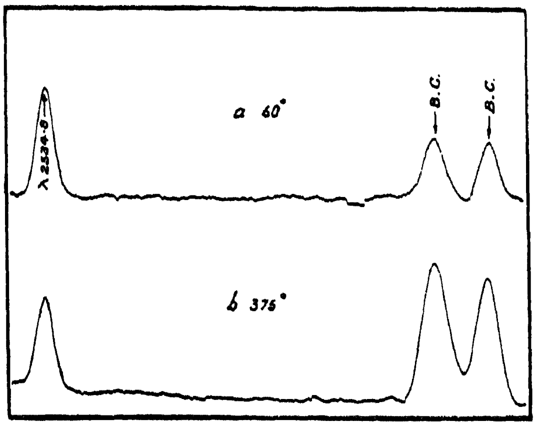

FIG. 6. Microphotometer records of the scattered spectrum of quartz at two different temperatures

6. FIRST ORDER RAMAN SPECTRUM

In Fig. 7 is reproduced the Raman spectrum of quartz taken with the three-metre spectrograph using a slit width of 0·035 mm. and an exposure of 7 days. Besides the two Brillouin shifts, 16 Raman lines were recorded in the scattered spectrum. Their positions and frequency shifts are marked in the figure. Of these, fourteen lines including two close doublets form the fundamental modes of oscillation of the unit cell of quartz (Krishnan, 1945). The new feature in the spectrum recorded with the high dispersion instrument is the appearance of a low frequency line at 26 cm.$^{-1}$ which has been recorded for the first time. This should be attributed to one of the super lattice frequencies of the quartz structure. The line at 452·2 cm.$^{-1}$ can be seen clearly separated from the intense line at 466 cm.$^{-1}$. It was not so in the case of the spectrum taken with the El quartz spectrograph (Krishnan, 1945).

Three most intense Raman lines, namely, 127·7, 206·4 and 466, exhibit appreciable width. The total width in cm.$^{-1}$ of fourteen Raman lines as measured from the spectrogram are shown in brackets against the respective frequency shifts: 26 (10), 127·7 (10), 206·4 (40), 266·1 (6), 357·2 (6), 394·8 (4), 403·8 (6), 452·2 (6), 466 (20), 696·4 (7), 794·7 (6), 805·8 (8), 1063·7 (6) and 1159·3 (8).

7. SUMMARY

Using the λ 2536·5 mercury resonance radiation and a three-metre quartz spectrograph, the fine structure of the thermal scattering of light in crystalline quartz has been investigated. The scattered spectrum exhibits only one pair of Doppler-shifted or Brillouin components due to the longitudinal sound waves in the medium. The observed frequency shift is in good agreement with the value calculated from the known elastic constants of quartz. The dependence of the frequency shift of the Doppler components on the orientation of the crystal with reference to the directions of incidence and scattering has been quantitatively verified for seven different settings of the crystal. The temperature variations in intensity of the shifted components has also been investigated and is found to be in accordance with the theory of scattering.

In the first order Raman spectrum, a new Raman line with a frequency shift of 26 cm.$^{-1}$ has been recorded.

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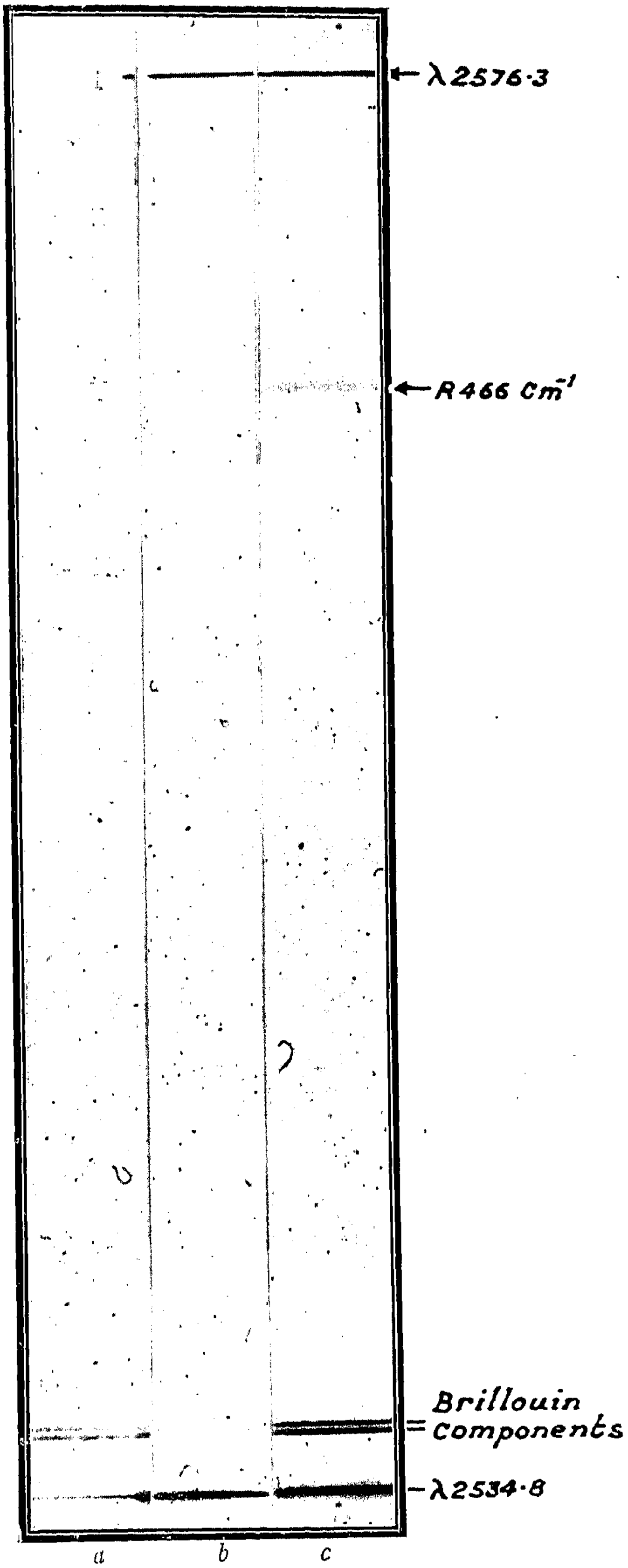

FIG. 1. (*a*) and (*c*) the spectrum of the scattered light in quartz taken with the three metre spectrograph after absorption in mercury vapour
(*b*) comparison mercury spectrum after absorption in mercury vapour

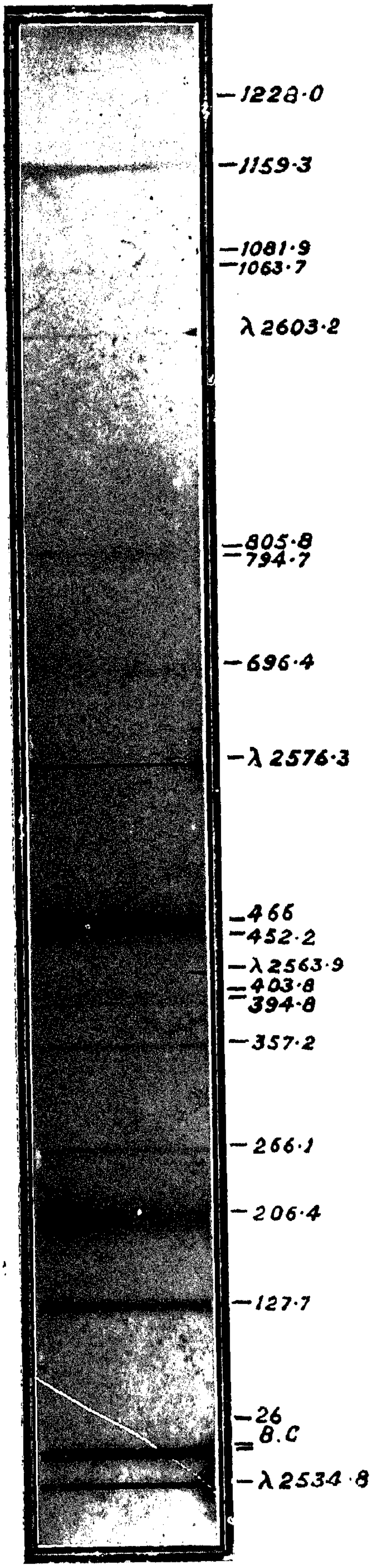

FIG. 7. First order Raman spectrum of quartz taken with the three metre spectrograph

FIG. 2. Filtered mercury spectrum G=ghost W=wing

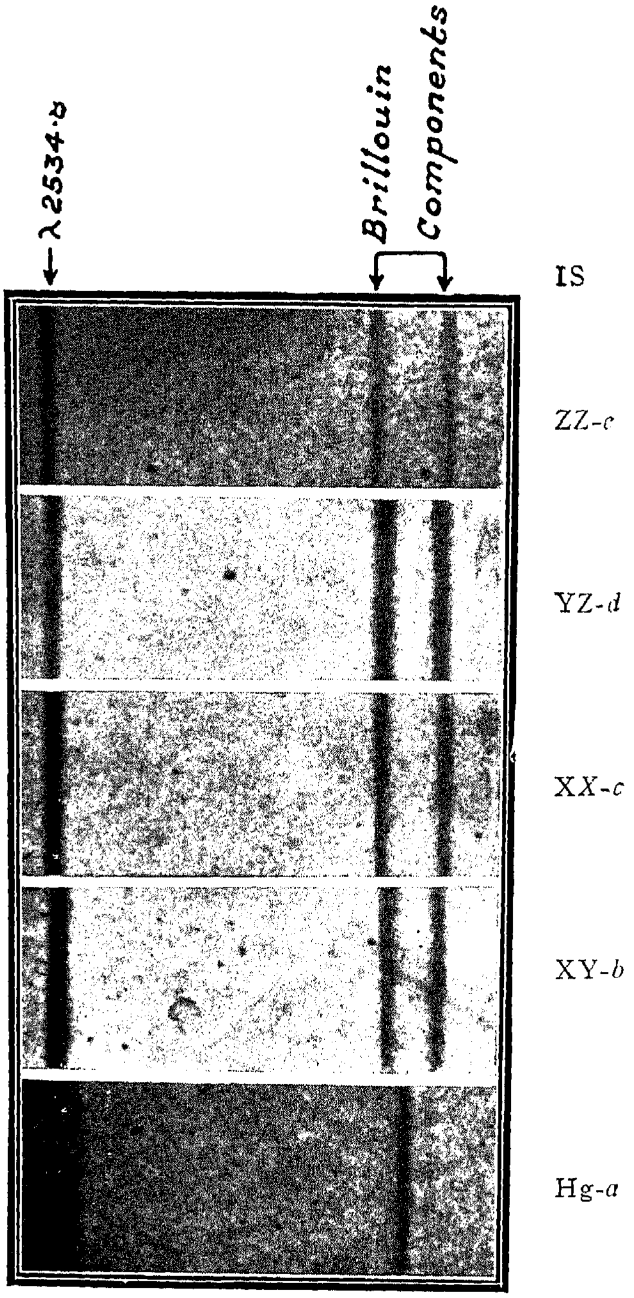

FIG. 4. *a*—heavily exposed filtered mercury spectrum (*b*) to (*e*) Scattered spectrum of quartz for four different orientations

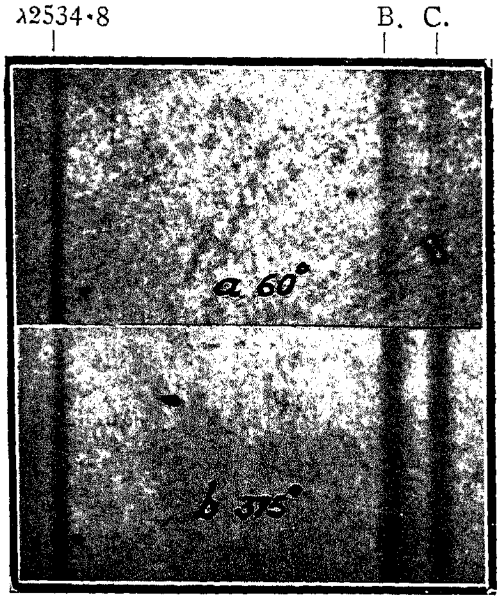

FIG. 5. Scattered spectrum of quartz taken with the crystal maintained at two different temperatures