

RAMAN SPECTRUM OF ALUMINA AND THE LUMINESCENCE OF RUBY

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1. INTRODUCTION

A STUDY of the Raman effect in alumina is of much theoretical interest as its vibration spectrum plays an important role in the luminescence and absorption spectra of minerals in which alumina forms the ground material. Hibben (1932) who was the first to examine the spectrum of alumina reported the existence of four weak Raman lines. However, the values of the frequency shifts given by him were not in agreement with those reported by the later investigators. In order to find an explanation for the numerous bands appearing in the luminescence and absorption spectra of ruby, Deutschbein (1932 *b*) photographed the Raman spectrum of alumina. He could observe only a single Raman line at 415 cm.^{-1} . Besides confirming the result of Deutschbein, Miss Mani (1942) reported the existence of an additional line at 376 cm.^{-1} . In a subsequent unpublished investigation, the same author recorded other faint lines in the spectrum of alumina besides the two already reported, among which two with frequency shifts 752 and 633 cm.^{-1} appeared most definite. Both Deutschbein and Miss Mani employed the $\lambda 4046$ and $\lambda 4358$ radiations of the mercury arc for exciting the Raman spectrum of alumina which is comparatively very feeble. It is not surprising therefore to note that no spectrograms have been reproduced by these authors. Moreover, the results obtained by them are far from being complete, for, from group theoretical analysis, Bhagavantam has shown that alumina should have seven Raman active frequencies. In view of this, it appeared desirable to re-examine the Raman spectrum of alumina using a more powerful technique than the one employed by the earlier workers. A detailed study of the scattering of light and the Raman effect in alumina has therefore been made using the $\lambda 2536.5$ mercury resonance radiation as exciter, and valuable results have been obtained. A preliminary report of the same has appeared in *Nature* (Krishnan, 1947). Further details are presented in this paper together with a discussion of the significance of the results in relation to the luminescence spectrum of ruby.

2. EXPERIMENTAL DETAILS AND RESULTS

While attempting to record the Raman spectrum of colourless synthetic alumina using the $\lambda 2536.5$ radiations, Roop Kishore (1942) found that the sample acquired a yellow colouration and became phosphorescent emitting a green radiation for a long time. The sample which was transparent to the 2536.5 radiations before the exposure, became practically opaque afterwards. Although the present writer confirmed the observations of Roop Kishore, it was found that certain specimens of synthetic alumina did not become coloured and opaque under ultra-violet irradiation. A large boule of synthetic alumina presented to Sir C. V. Raman by the Linde Air Products Co. of New York, belonged to this variety and was therefore chosen for the present study. It was in the form of a cylinder (6 cm. long and 2 cm. in diameter) with one end flat and polished and the other end tapered. The boule was clamped horizontally and was illuminated through the side. The scattered light emerging through the flat end was focussed on the slit of the spectrograph.

Doppler-shifted or Brillouin Components.—Fig. 1(b) represents the spectrogram of the scattered light taken with a Hilger large quartz (E1) spectrograph. A slit width of 0.04 mm. and an exposure of about 15 hours were used. Fig. 1(e) represents the spectrogram of the incident radiation after quenching with a mercury vapour filter. The doubling of the 2536 line in the spectrum of the scattered light is clearly seen in Fig. 1(b). The same effect is shown in the microphotometer record reproduced in Fig. 1(c). The doubling is also clearly seen in the spectrogram taken with the medium quartz spectrograph and the microphotometer record reproduced in Fig. 1(d) and (a). As is well-known, this doubling is due to a kind of Doppler effect arising from the selective reflection of the monochromatic light by the approaching and receding sound waves of thermal origin in alumina. The two components are termed as Doppler-shifted or Brillouin components. This is the first time that the existence of sound waves of thermal origin in alumina has been demonstrated experimentally. Because of the high value of the velocity of sound in alumina next only to diamond, it has been possible to record the Brillouin components directly using a quartz spectrograph of moderate power without any interferometric aid.

The frequency shifts of the Brillouin components from the exciting line have been estimated as well as their widths. The mean shift is $\pm 2.45 \text{ cm.}^{-1}$, while the width of each component is of the order of 1.8 cm.^{-1} . Taking the refractive index of alumina to be equal to 1.8, the velocity of sound waves responsible for the Doppler shift has been evaluated from the well-known

Brillouin formula. The value comes to about 7300 meters/sec. The angle of scattering was nearly 90° and the optic axis of the specimen lay in the plane of scattering equally inclined to the directions of incidence and observation. Therefore, the calculated value of the velocity is for sound waves travelling along the optic axis. As only one pair of broad Brillouin components is recorded, it is not possible to say whether the transverse and/or longitudinal sound waves were effective. Since the incident light had necessarily to be a convergent beam in order to shorten the time of exposure, there was a finite range for the angle of scattering θ round a mean value of 90° . Besides, the velocities of sound waves change with direction in the crystal. All these factors have tended to broaden the components and to mask their structure.

No direct determination of the sound velocities in alumina exists for comparison with the value obtained by the optical method. Even the measurements of the elastic constants of alumina are very scanty. Only the elastic constant along the optic axis has been determined. The order of magnitude of the sound velocity has therefore been computed from a knowledge of the density ρ and the elastic constant E_0 of alumina along the optic axis using the approximate formula $v_l = \sqrt{\frac{E_0}{\rho}}$ where v_l = velocity of longitudinal sound waves. Putting $E = 5 \times 10^{12}$ dynes/cm.² and $\rho = 4$, the calculated value of the velocity is roughly 11,000 metres/sec. This is definitely higher than the value calculated from the mean shift of the Brillouin components. A possible explanation for this discrepancy is that each one of the Doppler shifted components is an unresolved combination of components arising from the longitudinal and transverse sound waves inside the medium and therefore the velocity calculated from the mean frequency shift should represent the mean of the velocities of the longitudinal and transverse sound waves. The value calculated from the elastic constant is for longitudinal sound waves.

It is interesting to compare the intensity of thermal scattering in alumina with that in diamond. For a depth of illumination equal to half a centimetre, the Brillouin components in diamond could be photographed with reasonable intensity in two minutes using the medium quartz spectrograph. In the case of alumina, on the other hand, for a depth of illumination of about 2 cm. in order to photograph the Brillouin components with the same intensity as in diamond, an exposure of two hours had to be given. This gives an idea about the extreme feebleness of the scattering in alumina. Unlike in diamond, the Brillouin components in alumina are more intense than the brightest Raman line (417 cm.^{-1}) of alumina (see Fig. 2 a).

Raman Spectrum.—The Raman spectrum of alumina taken with the medium quartz spectrograph and an exposure of one day is reproduced in Fig. 3 (a) together with a comparison spectrum of the mercury arc (Fig. 3c). The spectrum exhibits seven Raman lines. Their positions are indicated in the Figure along with the frequency shifts in wave numbers from the exciting line. The Raman lines are listed in Table I together with rough estimates of their relative intensities.

TABLE I
Raman Spectrum of Alumina

Serial No.	Frequency shift in cm.^{-1}	Relative intensity	Nature	Polarisation	Miss Mani (1942)
1	375	8	sharp	depolarised	376
2	417	10	sharp	depolarised	412
3	432	4	broad	depolarised	..
4	450	1	sharp	polarised	..
5	578	3	sharp	polarised	..
6	642	6	broad	depolarised	633
7	751	7	broad	polarised	752

The lines with frequency shifts 375, 417 and 642 cm.^{-1} fall on or adjacent to the mercury lines $\lambda 2561.2$, $\lambda 2563.9$ and $\lambda 2578.4$ respectively. But there is no difficulty in identifying them as two of them appear prominently on the anti-Stokes side, while the existence of the third is made certain by comparing the scattered spectrum with the spectrum of the direct arc. The Raman lines are clearly seen in the spectrogram taken with the large quartz E1 spectrograph and reproduced in Fig. 2 (a).

In order to determine the polarisation characteristics of the Raman lines for incident unpolarised light, a quartz double image prism with its axes horizontal and vertical and an ultra-violet transparent nicol with its principal plane inclined at angle of 45° to the vertical were interposed in the path of the scattered beam between the crystal of alumina and the condensing lens. The optic axis of the crystal was nearly parallel to the direction of observation. The resulting spectrogram is reproduced in Fig. 3 (b). The lines with frequency shifts 450, 578 and 751 appeared with greater intensity in the vertical component, indicating thereby that these lines are polarised, while the remaining ones are depolarised.

3. THE INFRA-RED SPECTRUM

Studies on the infra-red absorption and reflection spectra of alumina are very scanty. Coblenz (1908), who was the first to investigate the case, reported three maxima in selective reflection at 11μ , 11.8μ and 13.5μ

corresponding to the frequency shifts of 909, 847 and 741 cm.^{-1} Strong (1931) who investigated the reflectivity of alumina for specific wave-lengths in the region 20–150 μ , deduced three reflection maxima, a very strong one at about 23 μ (434 cm.^{-1}), a broad and less intense one between 27 μ and 29.5 μ and a very weak one at about 52 μ (192 cm.^{-1}). Recently, Parodi (1937), while examining the transmission of oxides in the far infra-red, reported the existence of three maxima of absorption in corundum at 30.5 μ (328 cm.^{-1}), 41 μ (244 cm.^{-1}) and 51.5 μ (194 cm.^{-1}). As reflections are generally observed on the shorter wavelength side of the corresponding absorption, it is reasonable to assume that the reflection peak between 27 μ and 29.5 μ reported by Strong and the absorption at 30.5 μ reported by Parodi are due to one and the same mode of oscillation of the lattice. Taking this into consideration, one observes in all six infra-red frequencies at 194, 244, 328–355, 434, 847 and 909 cm.^{-1} . The values are only approximate as some of them represent positions of reflection maxima. The reflection maximum at 13.5 μ (741 cm.^{-1}) may be assigned as the octave of 375 cm.^{-1} . A detailed study of the infra-red absorption spectrum of alumina using thin specimens is desirable.

4. DISCUSSION OF RESULTS

The crystal structure of alumina is similar to that of calcite, the space group being D^6_{3d} . The unit cell is a rhombohedron containing two molecules. A group theoretical analysis of the normal modes of oscillation of the alumina lattice has been carried out by Bhagavantam and Venkatarayudu (1939). The main results are summarised in Table II.

TABLE II

P = permitted to appear ; F = forbidden.

Class	No. of Modes	Raman	Infra-red	Observed frequencies in cm.^{-1}
A_1 ..	2	P	F	578, 751
A_2 ..	3	F	F	
B_1 ..	2	F	P	244, 847
B_2 ..	2	F	F	
E_1 ..	4	F	P	194, 328–355, 434, 909
E_2 ..	5	P	F	375, 417, 432, 450, 642

Of the 18 normal modes of oscillation with distinct frequencies, 7 are permitted to appear in Raman effect, 6 in infra-red absorption and the rest inactive in both. Consequently, there will not be any coincidence between the Raman and infra-red frequencies. Of the seven Raman-active frequencies, two come under the symmetric class and the rest under degenerate class. It is satisfactory to note that the Raman spectrum of alumina exhibits

seven frequency shifts in accord with the theoretical work of Bhagavantam and Venkatarayudu. Taking into consideration the state of polarisation and intensities of the Raman lines, the frequency shifts 578 and 751 cm.^{-1} have been assigned to class A_1 and the rest to class E_2 . Provisional assignments have also been made for the six infra-red frequencies. Further detailed assignment of the frequencies to the particular mode or modes contemplated by Bhagavantam and Venkatarayudu has not been made for two reasons. Firstly, data on the dependance of the Raman lines on the crystal orientation are lacking and secondly, the dynamics of the system has not been fully worked out.

5. LUMINESCENCE SPECTRUM OF RUBY

The foregoing results are of interest in relation to the luminescence and absorption spectra of ruby which, as is well-known, is crystalline alumina with chromic oxide impurity present as a colouring agent. Ruby is one of the most frequently examined substance in luminescence studies. The earliest investigations were those of du Fay (1724), Boisbaudran (1887), Crookes (1887, 1889), Miethe (1907), du Bois and Elias (1908), Becquerel (1907, 1910, 1911) and Mendenhall and Wood (1915). Recently, the subject has been studied by Deutschbein (1932 *a*, *b*, 1934), Venkateswaran (1935), Thosar (1938, 1941, 1942, 1944) and Miss Mani (1942). The investigations of Deutschbein and of Miss Mani were carried out with some thoroughness. As Deutschbein worked at liquid air temperature also, detailed reference is made here to the results reported by him. The emission and absorption spectra of ruby at 20° C. and - 195° C. are schematically represented in the accompanying chart (Fig. 4) which is taken from Deutschbein's (1932 *a*) paper.

The main features can be summarised as follows:—At room temperature, the luminescence spectrum consists of two sharp and intense lines λ 6927 and λ 6942 respectively, accompanied by other bands of varying width and intensity both on the longer and shorter wave-length sides of the principal doublet. These extend from λ 6583 to λ 7921. At liquid air temperature, the bands on the shorter wave-length side of the principal doublet disappear completely from the fluorescence spectrum. At low temperatures there is no correspondence between the fluorescence and absorption bands except in regard to the principal doublet and a few fairly sharp companion lines appearing on the longer wave-length side of the principal doublet and extending up to λ 7049.

It is now an accepted fact that the electronic transitions of the triply ionised chromium ions are responsible for the two principal intense lines

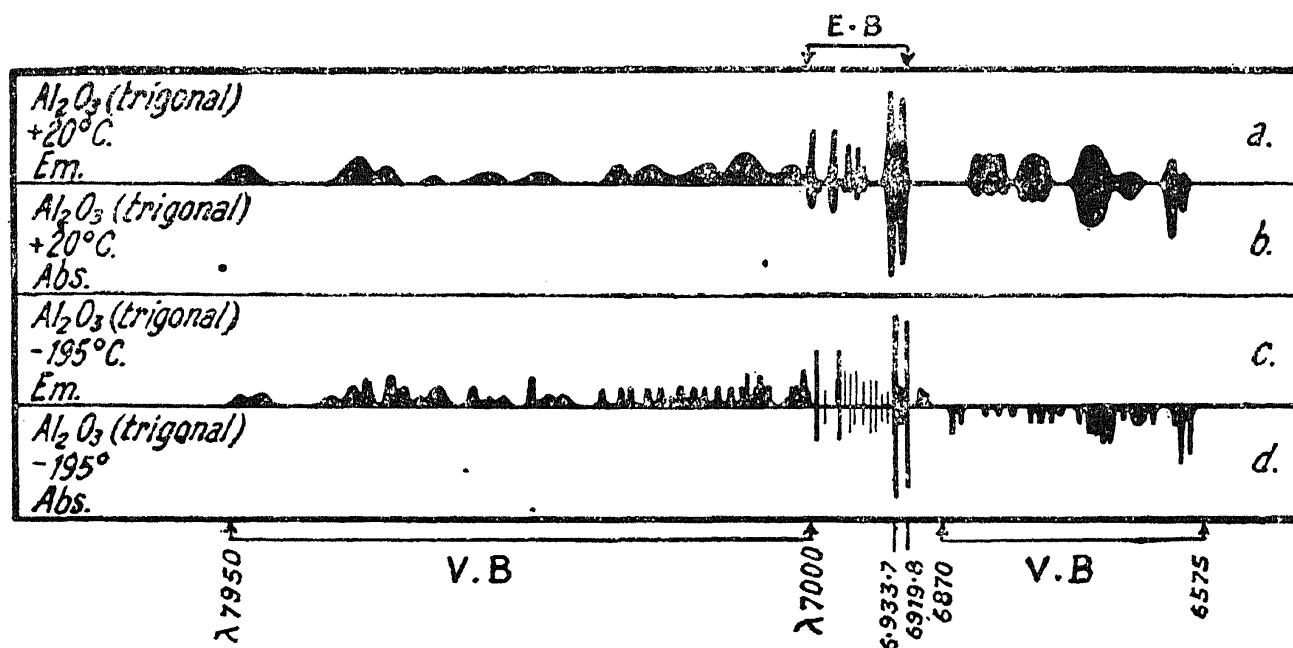


FIG. 4. Chart showing the emission and absorption spectra of ruby reproduced from Deutschbein's paper (1932).

V.B = vibrational bands, E.B = electronic bands.

at $\lambda 6927$ and $\lambda 6942$, as well as the fainter lines in the region $\lambda 6927-7049$ appearing at the same position in luminescence and absorption. Regarding the origin of the bands which lie on either side of the group of electronic bands ($\lambda 6927-7049$), Deutschbein was the first to suggest that these might arise from the combination of the vibration frequencies of the alumina lattice with the electronic transitions of Cr^{+++} ions. As he observed only one Raman shift (412 cm.^{-1}), he explained the fluorescence band at 7138 A.U. as due to this frequency. Miss Mani (1942), who reported four Raman lines, satisfactorily accounted for eight of the vibrational fluorescence bands on the Stokes and anti-Stokes sides of the principal doublet as due to the modulation of the electronic transitions by the crystal lattice vibrations. As the author has succeeded in recording the complete Raman spectrum of alumina, it is now possible to give more complete and satisfactory assignments for most of the vibrational bands of ruby than had been done by the earlier workers. Table III gives the list of all the vibrational bands observed by Deutschbein both in absorption and emission at -195°C. The bands at $\lambda 6596$, $\lambda 6680$ and $\lambda 6694$ appearing in absorption spectrum have been omitted from the table as there are no corresponding bands in the luminescence spectrum.

On the basis of the seven Raman frequencies listed in Table I, 8 absorption bands on the anti-Stokes side of the principal doublet and 13 luminescence bands on the Stokes side have been quantitatively accounted for. The corresponding assignments are given in Table III. It is interesting to note that while the more intense principal line R_1 ($\lambda 6933.7$) of chromium is responsible for the majority of the vibrational bands, there are some bands

TABLE III
Vibrational Bands of Ruby appearing in Luminescence and Absorption Spectra at - 195° C.
Emission

Ser. No.	Wave length in A.U.	Wave number in cm. ⁻¹	Intensity	Width	Shift in cm. ⁻¹ from λ 6933.7, R ₁	Shift in cm. ⁻¹ from λ 6919.8, R ₂	Assignments from lattice spectrum
Absorption							
1	6574.5	15208	5	10		761	751 R
2	6586.1	15179	6	10	761		751 R
3	6620	15101	2	10	683		ν_9
4	6640	15056	2	45	638		642 R
5	6654	15025	2	10		578	578 R
6	6672	14984	4	8	566		578 R
7	6688	14948	3	8	530		ν_8
8	6707	14906	2	10	488		ν_7
9	6729	14858	1	10		411	417 R
10	6744	14825	2	10	407		417 R
11	6757	14796	2	10	378		377 R
12	6768	14771	2	10	353		ν_6
13	6790	14724	1	10	306		ν_5
14	6807	14686	1	10	268		ν_4
15	6823	14652	1	10	234		ν_3
16	6854	14586	2	8	168		ν_2
17	6866	14561	3	6	143		ν_1
	6919.8	14447	9	3			Principal line R ₂
	6933.7	14418	10	4			Principal line R ₁
Emission							
1	7001.8	14278	4	3	140		ν_1
2	7012.5	14256	2	3	162		ν_2
3	7058.2	14164	3	5	254		ν_3
4	7067.4	14146	1	10	273		ν_4
5	7075.7	14129	1	10	289		2 ν_1
6	7082	14116	0	8	302		ν_5
7	7105.2	14070	1	7		377	375 R
8	7110.5	14060	1	7	358		ν_6
9	7120.0	14041	3	8	377		375 R
10	7124.3	14033	2	8		414	417 R
11	7131.6	14018	1	8		427	432 R
12	7139.6	14003	3	8	416		417 R
13	7145.9	13990	2	8	428		432 R
14	7161.3	13960	2	12	458		450 R
15	7178.1	13928	2	9	491		ν_7
16	7196	13893	2	10	525		ν_8
17	7211	13863	2	10		584	578 R
18	7231	13825	2	10	593		578 R
19	7245	13799	1	10		648	642 R
20	7260	13770	2	14	648		642 R
21	7279	13735	2	14	683		ν_9
22	7303	13689	2	12		758	751 R
23	7318	13661	2	14	757		751 R
24	7346	13609	2	14	809		ν_{10}
25	7404	13503	1	20	915		ν_{11}
26	7428	13458	1	20	960		375 + 578 R
27	7452	13415	3	10	1003		417 + 578 R
28	7494	13340	1	18		1107	
29	7514	13304	1	18	1114		
30	7538	13262	2	18	1156		2 × 578 R
31	7595	13163	2	50	1255		
32	7627	13108	1	20	1310		
33	7649	13070	1	18			
34	7669	13036	3	18	1382	1377	642 + 751 R
35	7709	12968	3	15	1450		
36	7739	12918	2	20	1500		2 × 751 R
37	7770	12866	1	40	1552		
38	7890	12670	1	60	1748		
39	7926	12613	1	60	1805		

R in column 8 represents that the particular frequency shift is observed in Raman spectrum.

which arise from the modulation of the less intense principal line R_2 (λ 6919.8). As is to be expected, the bands arising from the latter are less intense than those arising from the former. More or less perfect mirror image symmetry about the principal line R_1 (λ 6933.7) holds for the 9 bands λ 6866, 6854, 6823, 6807, 6790, 6768, 6707, 6688 and 6620 on the anti-Stokes side and for the bands λ 7001.8, 7012.5, 7058.2, 7067.4, 7082, 7100.5, 7178.1, 7196 and 7279 on the Stokes side. The corresponding vibrational frequencies are denoted by $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6, \nu_7, \nu_8$ and ν_9 . The vibrational frequencies corresponding to the emission bands λ 7346 and λ 7404 are taken as ν_{10} and ν_{11} . These eleven frequencies represent the remaining eleven normal modes of oscillation of the alumina lattice which include the six infra-red active frequencies also. As the values of the latter are not known accurately, no attempt has been made to assign some of the bands mentioned above as arising from the modulation by particular infra-red frequencies. ν_3, ν_6, ν_{10} and ν_{11} may be identified with the infra-red frequencies 244, 328-355, 847 and 909 cm.^{-1} respectively. There is a group of 14 bands appearing on the Stokes side in the region λ 7428-7926 which are yet to be accounted for. There are no corresponding bands in the absorption spectrum. A possible explanation for the appearance of these bands is that they arise from the modulation of the electronic transitions of Cr^{+++} ions by some of the octaves and combinations of the vibration frequencies of the alumina lattice. Some of the more obvious assignments are indicated in column 8 of Table III.

In fluorescence and absorption, the lattice vibrations appear as diffuse bands and not as sharp lines. This is true even at low temperatures. The broadening can be explained on the basis that the loading of the lattice by the chromium ions gives rise to a perturbation of the vibrational modes. Part of the broadening may also be due to the fact that the principal electronic lines themselves have a finite width.

In conclusion, the author is grateful to Prof. Sir C. V. Raman for the loan of the specimens of alumina used in the present investigation and also for his kind interest in the work.

6. SUMMARY

Using the λ 2536.5 mercury resonance radiation as exciter, the scattering of light in crystalline alumina has been investigated. The spectrum of the scattered light exhibits two Doppler-shifted components centred round the exciting line and seven Raman shifts. From the measured shift of the Doppler components the velocity of sound in alumina has been estimated. The appearance of seven Raman lines is shown to be in accord with the

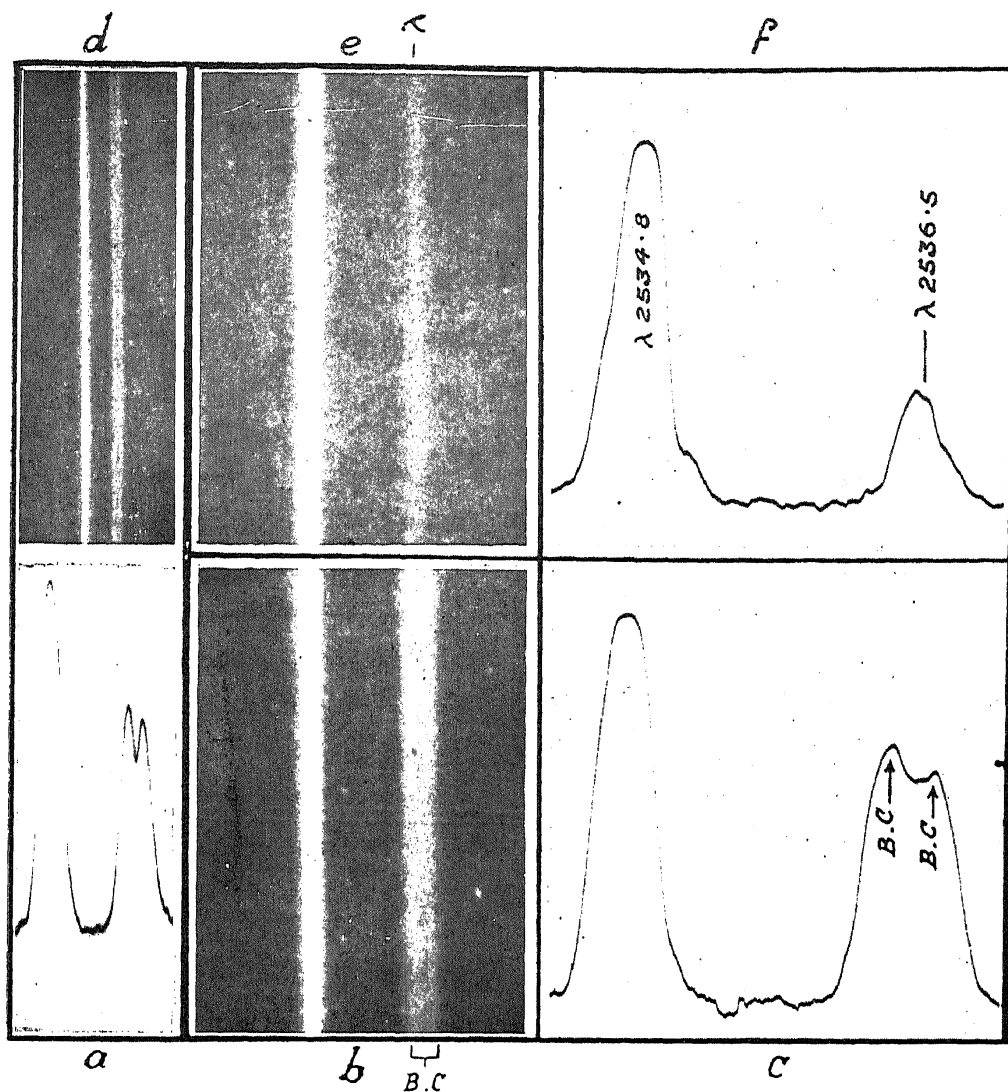
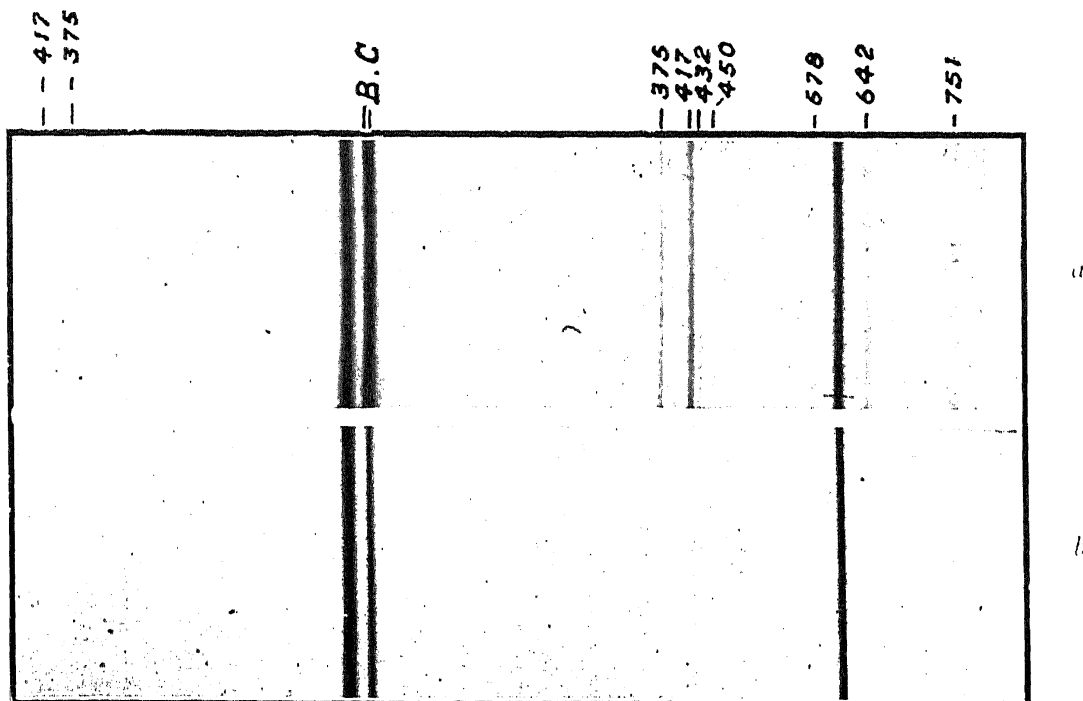


FIG. 1
 B. C. = Brillouin components
 $\lambda = 2536.5 \text{ A. U.}$



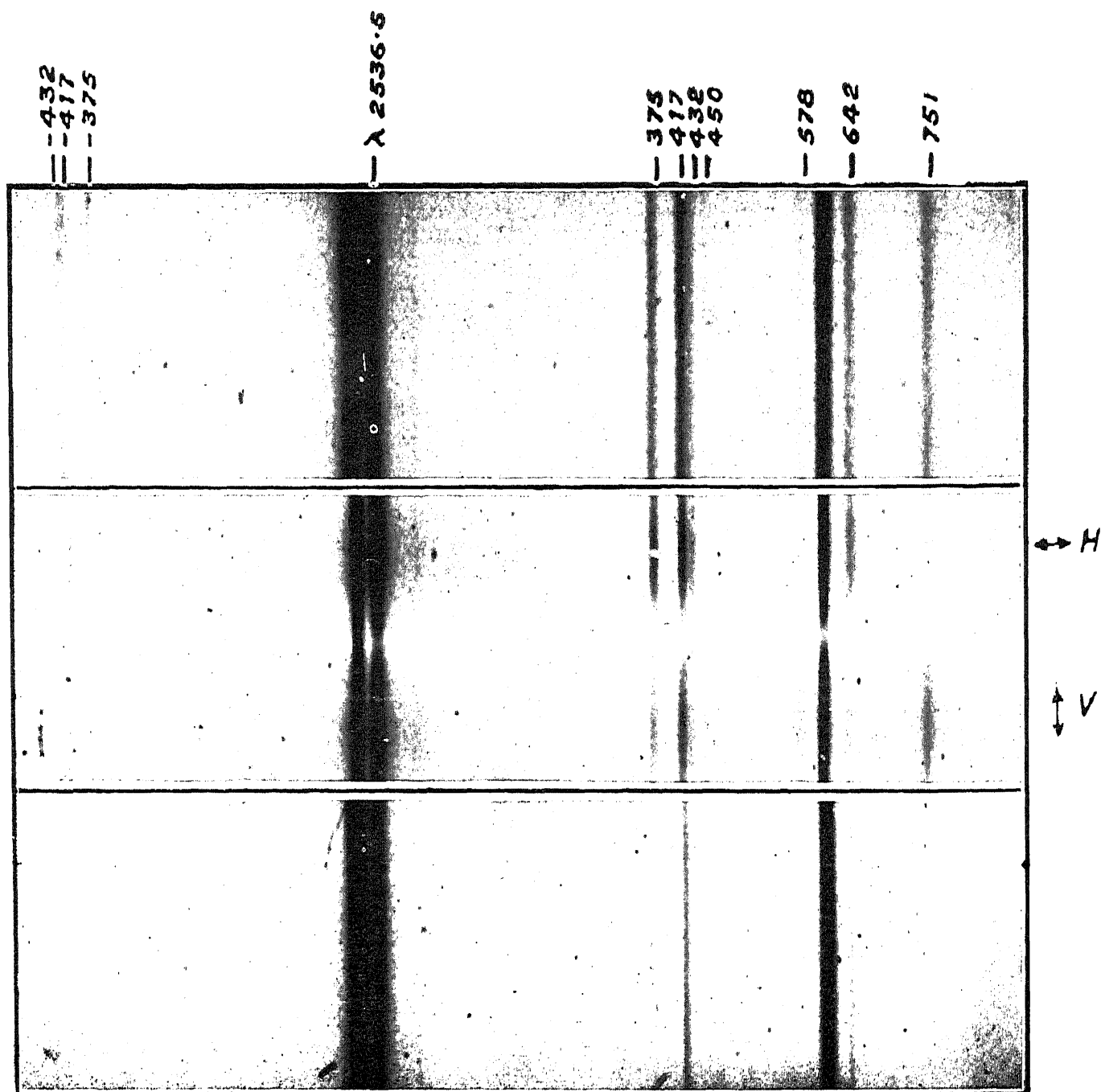


FIG. 3

H = horizontal component

V = vertical component

theoretical work of Bhagavantam and Venkatarayudu. The numerous bands appearing on both sides of the principal fluorescence doublet of ruby have been satisfactorily explained as arising from the combination of the vibration frequencies of the alumina lattice with the electronic transitions of the chromium ions.

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DESCRIPTION OF PLATES

PLATE XIX

- FIG. 1. (d) and (a) the spectrum of the scattered light in alumina taken with the E 3 spectrograph and its microphotometer record.
 (b) and (c) the same taken with the E 1 spectrograph and its microphotometer record.
 (e) and (f) mercury spectrum taken with the E 1 spectrograph and its microphotometer record.

- FIG. 2. (a) Raman spectrum of alumina taken with the E 1 spectrograph.
 (b) Comparison spectrum of the mercury arc.

PLATE XX

- FIG. 3. (a) Raman spectrum of alumina taken with the E 3 spectrograph.
 (b) The same taken with a double image prism and a nicol in the path of the scattered light.
 (c) Comparison spectrum of the mercury arc.