

# FLUORESCENCE, ABSORPTION AND SCATTERING OF LIGHT IN RUBY

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## 1. Introduction

THE fluorescence and the pleochroism exhibited by ruby have been the subject of detailed investigations at the hands of many investigators, notably du Fay (1724), Boisbaudran (1887), Crookes (1887, 1889), Miethe (1907), Becquerel (1907, 1910, 1911), Mendenhall and Wood (1915) and Gibson (1916). They have been studied with especial thoroughness by du Bois and Elias (1908) and by Deutschbein (1932, 1934). Reference may also be made to recent papers by Venkateswaran (1935) and Thosar (1938). The fluorescence spectrum consists at room temperatures of two sharp and intense lines at 6927 and 6942 A.U. respectively, accompanied by other bands of varying width and intensity. At ordinary temperatures, these appear at wavelengths longer and shorter than the principal doublet. But at liquid air temperatures the bands towards the shorter wavelength disappear completely from the fluorescence spectrum. At such temperatures, there is no correspondence between the fluorescence and absorption bands except in regard to the principal doublet and certain fainter companion lines which appear on the longer wavelength side of the same. In other words, the Stokes Law is strictly obeyed, only longer wavelength bands appearing in fluorescence and the shorter wavelength bands in absorption.

Despite the numerous investigations mentioned above, the fluorescence spectrum of ruby has not as yet been fully elucidated. The two principal lines are usually regarded as due to electronic transitions in the triply ionized chromium atoms present as an impurity in the crystal. This explanation leaves it obscure why the principal lines do not agree in position and intensity when the nature of the ground material is varied. The fainter components accompanying the principal doublet have been ascribed by Deutschbein to an intra-molecular Stark effect. Why, if this be the case, the companions appear only on the longer wavelength side is unexplained. Further, the diffuse bands have been attributed to the superposition of the molecular

or crystal lattice vibrations on the electronic transitions. This view, however, is unsupported by any independent data regarding the lattice spectrum of the crystal except in regard to one frequency nearly at  $415 \text{ cm.}^{-1}$ , which has been identified in the Raman spectrum of alumina, and agrees tolerably with the frequency shift of the 7138 band in fluorescence.

That the chromium activator forms an integral part of the crystal lattice of the ground material *viz.*, aluminium oxide, is indicated by the fact that the principal lines in emission and absorption are partially polarised (Pringsheim, 1928). Previous investigations on the polarised absorption and polarised excitation of fluorescence are however, confined to the principal doublet. A fuller study of the polarisation characters of the fluorescence and absorption bands as well as the Raman spectrum of the crystal has been carried out and is described in the present paper. The work was undertaken in order to elucidate the origin and nature of the principal, subsidiary and diffuse bands exhibited by ruby, as well as the nature of the arrangement of the  $\text{Cr}^{+++}$  ions in the ground lattice.

## 2. *The Lattice Spectrum of Alumina*

The Raman spectrum of alumina has been previously studied by Hibben (1932) who reported four weak lines having frequency shifts of 536, 728, 931 and  $1191 \text{ cm.}^{-1}$ , and by Deutschbein (1932) who could observe only one Raman line at  $415 \text{ cm.}^{-1}$ . Two large crystals of transparent synthetic alumina of dimensions  $3.5 \times 2 \times 1.5 \text{ cms.}$  and  $4 \times 2 \times 2 \text{ cms.}$  respectively were used in the present investigation. A two prism glass spectrograph supplied by Adam Hilger, having a dispersion of  $28 \text{ \AA/mm.}$  in the  $4358 \text{ \AA.}$  region was employed for photographing the spectra. The crystal was immersed in a liquid of nearly the same refractive index, *viz.*,  $\alpha$ -bromonaphthalene, to minimise parasitic illumination and diminish the strong continuum due to fluorescence. The spectrum recorded, however, was very weak even after two days of continuous exposure. Two Raman lines having frequency of  $412$  and  $376 \text{ cm.}^{-1}$  have been recorded with fair intensity on the plates. The line at  $412 \text{ cm.}^{-1}$  is stronger than the other. It may, however, be remarked that there are indications of the presence of a few more faint lines in the spectrum. But due to the superposition of the strong continuum, they cannot be listed with certainty.

Coblentz (1908) has reported three maxima in selective reflection for alumina at  $11 \mu$ ,  $11.8 \mu$  and  $13.5 \mu$  corresponding to frequency shifts of 909, 847 and  $741 \text{ cm.}^{-1}$  and it will be seen that they do not coincide with either of the observed Raman lines.

### 3. The Absorption Spectrum of Ruby

The absorption spectrum of the sample of ruby used for the study of fluorescence was obtained using a tungsten filament lamp as the source of continuous radiation. The crystal was placed with its optic axis perpendicular to the direction of observation so that light traverses the crystal in a direction perpendicular to the optic axis, and the ordinary and extraordinary spectra were recorded.

The absorption spectrum in the red consists of a doublet with three bands on the Stokes and six on the anti-Stokes side. The spectrum is reproduced in Fig. 5, and the relative intensities of the different bands in both spectra are given in Table I. It will be seen from a comparison of Tables I and II that the absorption bands correspond closely with those appearing in emission. In the extraordinary spectrum, with the electric vector vibrating along the optic axis, all bands except 6595 and 6693 are very weak. These results are in agreement with those of du Bois and Elias (1908). Three bands in the blue, ascribed by Deutschbein to  ${}^4F \rightarrow {}^2H$  transitions of  $Cr^{+++}$ , are also given in Table I, along with their intensities in the two spectra, and re-

TABLE I

#### *The Absorption Spectrum of Ruby*

No.	Wave-length	Wave-numbers	Intensities of bands	
			Ordinary	Extraordinary
1	6581	15191	..	..
2	6595	15158	6	5
3	6649	15036	..	..
4	6693	14937	5	2
5	6758	14793	2	0
6	6822	14654	2	0
7	6927	14431	9	2
8	6942	14400	10	1
9	6996	14290	1	0
10	7016	14249	1	0
11	7049	14182	1	0
12	4686	21334	2	6
13	4753	21033	5	1
14	4768	20967	3	5

produced in Fig. 6. The results show that two of these bands *viz.*, 4686 and 4768 A.U. are opposite in behaviour to those in the red region, the intensity of the extraordinary ray for them being greater than the ordinary. The strong

polarisation of these bands had been visually observed by du Bois and Elias.

#### 4. *The Fluorescence Spectrum of Ruby*

For the observations of the photo-luminescence of ruby, a piece of synthetic ruby,  $9 \times 7 \times 5$  mms. cut with its longest edge parallel to the optic axis was employed. The axis was fixed by observing the extinction directions between crossed polaroids and confirmed by viewing it in convergent light between crossed nicols, after cutting it. Light from a pyrex mercury arc was focussed on the crystal by a long-focus lens and the fluorescence spectrum photographed with a Fuess glass spectrograph having a dispersion of nearly  $100 \text{ \AA/mm.}$  in the 6900 A.U. region. The fluorescent light emitted transversely to the incident beam was focussed on the slit of the spectrograph. In experiments with polarised light, a properly oriented nicol was placed between the crystal and the incident beam and a double-image prism was inserted in the path of the fluorescent light. Ilford H.P.2 plates having an H and D number of 2500, and Ilford infra-red plates with H and D 100, sensitized with ammonia were used in photographing the spectra. Wavelengths of the bands were ascertained by measurements with a cross-slide micrometer in comparison with neon lines as standard.

Table II gives the wavelengths and intensities of the bands obtained along with those given by Deutschbein and Venkateswaran. Besides the twenty-four bands observed by Deutschbein, three new bands with centres approximately at 7539, 7544 and 7772 A.U. have been recorded. Further the 7138 band shows a definite doublet structure with components at 7129 and 7147 A.U. respectively. Because of the insensitiveness of the infra-red plates used to the 6000–6900 A.U. region, the bands 6495 and 6430 observed by Venkateswaran could not be obtained. The author's values show fairly good agreement with the rest, considering the low dispersion of the instrument used. It should, however, be remarked that the bands on the Stokes side appear to be sharper in the ruby used in the present investigation than those recorded by Deutschbein. Their intensities as compared with the principal lines also show differences from those given by the latter. The complete fluorescence spectrum of ruby is reproduced in Fig. 1 in the accompanying Plate.

TABLE II

*The Fluorescence Spectrum of Ruby*

Author—25° C.		Deutschbein—20°			Venkateswaran—35°
Wave-length	Intensity	Wave-length	Intensity	Half-width in $\text{cm}^{-1}$	Wave-length
5900-6700	..	..	..	..	6100-6900
..	..	..	..	..	6430
..	..	..	..	..	6495
6581	1	6583	1	30	..
6595	2	6595	3	40	6592
6649	1	6647	1	50	6650
6693	4	6692	4	80	6690
6758	3	6762	3	70	6753
6802	3	..	..	..	6791
6817	3	6820	3	100	6814
6833	2	..	..	..	..
6927	9	6927	9	16	6927
6942	10	6942	10	19	6945
6978	1	6977	2	18	..
6985	2	6986	4	18	..
6996	2	6996	4	18	6992
7016	4	7017	6	18	7027
7049	6	7049	6	18	7059
7078	6	7072	2	60	7089
7129	7	..	..	..	7125
7147	7	7138	3	60	..
7188	6	7188	2	80	7164
..	..	..	..	..	7222
7275	5	7276	2	60	7266
7324	4	7323	2	60	..
7359	2	..	..	..	..
7440	1	7438	1	100	..
7520	2	7517	1	100	..
7544	2	..	..	..	..
7606	1	7603	1	40	..
7674	1	7675	2	40	..
7725	3	7723	3	100	..
7772	2	..	..	..	..
7924	2	7921	2	100	..

5. *Polarisation of the Fluorescence Bands*

Designating the three mutually perpendicular directions in space as OX, OY and OZ, where OX is the direction of incidence, OY the direction of observation and OZ the vertical direction perpendicular to the other two, the crystal is set with its optic axis along any one of the three directions for studying the polarisation characters of the bands. For each of the three settings, three separate photographs were taken,

(1) with incident light unpolarised,

(2) with incident electric vector polarised with vibrations along OZ,  
and

(3) with incident electric vector polarised with vibrations along OY. The fluorescent light was analysed into vertical (OZ) and horizontal (OX) components by means of a double-image prism, and are marked V and H in the figures. The spectra obtained are illustrated in Figs. 2, 3, 4, 7, 8, 9, 10, 11 and 12 in the accompanying Plates.

(a) Figs. 2, 3 and 4 give the horizontal and vertical components for unpolarised incident light where the optic axis is respectively along OX, OY and OZ.

(b) Figs. 7 and 8 illustrate the spectra with the optic axis along OX and the incident light vector along OY and OZ respectively.

(c) Figs. 9 and 10 correspond to the same setting as for *b*, but with the optic axis along OZ.

(d) Figs. 11 and 12 correspond to the same setting as for *b*, but with the optic axis along OY.

The directions of the optical vibrations in the incident light and the fluorescent light are indicated, when along OX and OY, by arrows parallel to them and by circles with central dots when along OZ. The optic axis is indicated by a set of three lines parallel to OX and OY when along them and by a triangle with a central dot when along OZ. Taking 20 as the intensity of the strongest band in each plate, intensities of the strong bands have been visually estimated and are given in Table III.

It will be seen from all the figures, that the principal doublet and almost all the bands are very intense when the fluorescent light vector vibrates in the (0001) plane, perpendicular to the optic axis; *i.e.* in general, the ordinary fluorescence spectrum is stronger than the extraordinary. Moreover, as may be seen from Figs. 7-12, both vertical and horizontal components appear brighter when the incident light vibrates perpendicular to the optic axis than when along it. This becomes intelligible when it is remarked that the absorption of light by ruby is also stronger for vibration-directions perpendicular to the optic axis. Figs. 2, 11 and 12 illustrate the fact that whatever the nature of polarisation of the incident light, with the crystal oriented with its optic axis along OY, both V and H components are equally intense for all the bands. This should be so, because for this particular orientation of the crystal, both components of the fluorescent light vibrate in the (0001) plane. However, the most remarkable fact is that with the incident light vector vibrating along

TABLE III  
*The Intensities of the Fluorescence Bands in Polarised Excitation*

Direction of vibration of Incident Light	Orientation of the Optic Axis along	Components of Fluorescent Light along	Relative Intensities of the Components of the Fluorescence Bands																
			6595	6693	6758	6822	6927	6942	7016	7049	7078	7129	7147	7188	7275	7324	7520	7725	7924
YZ Plane	OX	OX	2	1	2	2	12	10	4	4	4	7	8	5	7	4	3	3	2
	OZ	OZ	4	5	3	3	17	20	8	7	10	10	7	7	6	1	1	2	1
YZ Plane	OZ	OX	4	6	4	3	17	20	9	11	7	8	8	8	7	4	1	4	4
	OZ	OZ	2	2	2	2	12	10	5	8	5	8	5	6	6	2	4	4	1
OZ	OX	OX	1	1	2	2	12	10	4	4	4	8	4	6	6	2	2	1	1
	OZ	OZ	2	5	3	3	17	20	8	7	3	9	7	7	6	1	1	2	2
OZ	OZ	OX	3	5	3	3	17	20	8	7	7	9	8	8	5	3	3	3	2
	OZ	OZ	2	1	2	2	12	10	3	3	4	7	6	4	3	3	4	4	3
OY	OX	OX	1	1	2	2	12	10	4	4	4	8	5	6	5	3	3	2	2
	OZ	OZ	2	4	2	2	17	20	7	9	6	9	7	7	6	1	2	3	1
OY	OX	OX	3	5	3	3	17	20	8	7	7	10	7	7	5	1	4	4	2
	OZ	OZ	2	1	2	2	10	8	4	10	4	7	6	4	3	3	3	3	3

the optic axis, it is the component in fluorescence perpendicular to the optic axis that appears stronger. This may be clearly seen from Fig. 10. In general, whether the incident light vector vibrates along or perpendicular to the optic axis, it is that component vibrating perpendicular to the optic axis that comes out more intensely.

## 6. Discussion of Results

*A. The Lattice Spectrum of Alumina.*—According to detailed X-ray analysis, the crystal structure of alumina (corundum) is similar to that of calcite, and the unit cell belongs to the space group  $D_{3d}^6$  of the holohedral class of the rhombohedral system, having three equal axes making an angle of  $85^\circ 42'$  with each other. For the purpose of analysing the lattice spectrum of the crystal, we shall consider the fundamental unit cell containing four aluminium and six oxygen atoms. The character table for this is identical with that given by Bhagavantam and Venkatarayudu (1939), and indicates that the thirty degrees of freedom of the atoms are distributed among six representations, four of which are single and two doubly degenerate. Two vibrations of the totally symmetric class and five of the doubly degenerate types are active in the Raman effect, the same being inactive in the infra-red. Besides these seven, there are eleven modes of vibration, nine of which are active in the infra-red and two inactive in both the infra-red and the Raman spectra. Only three of the former have been observed in infra-red absorption.

One of the important facts emerging from the investigations of the Raman spectrum of alumina is its extreme feebleness in spite of the fact that a clear, transparent crystal of large size was available. It has been shown by several authors that the Raman lines connected with ionic bindings are generally of very low intensity. Therefore, the observed weakness of the spectrum of alumina rather suggests that the binding between Al and O atoms is more or less ionic in character.

The strongest of the Raman lines recorded, *viz.*,  $412 \text{ cm.}^{-1}$  is presumably due to one of the two totally symmetric oscillations of the unit cell considered above in which the two aluminium and the three oxygen atoms situated around the cell corners, move towards or away from their common centre.

*B. Electronic Transitions of Triply Ionized Chromium.*—All chromium phosphors give emission lines in the red, indicating that the lines owe their origin to the chromium activator embedded in the ground lattice isomorphically. Deutschbein (1932) has shown that these characteristic lines of chromium undergo significant changes in wavelength and intensity, with different

metallic oxides and silicates as the basic material. This is also evident from Venkateswaran's work (1935) on emerald (beryllium aluminium silicate) whose principal doublet coincides not with the 6927 and 6942 A.U. bands but with 6802 and 6822 A.U. bands of ruby. This suggests that the 'subsidiary' lines *viz.*, 6802, 6822, 6978, 6985, 6996, 7016 and 7049 together with the principal doublet of 6927 and 6942 A.U. in ruby, are due mainly to electronic transitions of the  $\text{Cr}^{+++}$  ion. The ground material has thus the effect of suppressing some of the electronic bands and enhancing some others. The principal doublet has been assigned to a transition  ${}^4F \rightarrow {}^2G$  of a  $3d$  electron of triply ionized chromium. Deutschbein assumes that the subsidiary bands arise from an intramolecular Stark effect. Candler (1937) has however, pointed out the difficulties inherent in the latter suggestion as it does not explain either the position or the differential intensities of the bands on either side of the doublet. Thosar (1938) has given reasons to believe that the 7016 and 7049 bands have frequencies that agree with the electronic transitions  ${}^4P_{5/2} \rightarrow {}^4F_{5/2}$  and  ${}^4P_{7/2} \rightarrow {}^4F_{7/2}$  of the  $\text{Cr}^{+++}$  ion respectively. The assignments of these bands to electronic transitions of  $\text{Cr}^{+++}$  ion is also supported by the observation that the fluorescence and absorption bands in the region 6927-7049 overlap.

*C. Vibrational Bands of Ruby.*—The important role played by the lattice of the ground material in the fluorescence and absorption spectra of ruby becomes clear when we consider the origin of the bands which lie on either side of the electronic bands in ruby. The present investigation shows that at room temperature the Stokes bands are distinctly stronger than the corresponding anti-Stokes bands. The observation of some authors that the anti-Stokes bands are stronger, is obviously due to the insensitiveness of the plates used by them to the longer wave-length region. The relative intensities of the Stokes and anti-Stokes bands observed in the present investigation suggest that they arise from the superposition of the lattice vibrations of alumina on the electronic transitions. Deutschbein was the first to suggest that these bands might arise thus and he explained the band at 7138 A.U., as due to the Raman frequency of  $412 \text{ cm.}^{-1}$  observed by him, being superposed on the electron jump. It has been shown earlier that there are altogether eighteen normal modes of vibration for the alumina lattice which may modulate the electronic transitions and give rise to fluorescence bands. On the basis of the two Raman frequencies at  $412$  and  $376 \text{ cm.}^{-1}$  and the three infra-red frequencies at  $909$ ,  $847$  and  $741 \text{ cm.}^{-1}$ , eight fluorescence bands on the Stokes and anti-Stokes sides of the principal doublet may be satisfactorily accounted for. These assignments are given in Table IV. A perusal of Table IV and the accompanying Plates, shows that more or less perfect mirror

TABLE IV

Wave-length in A.U. at 25° C.	Wave-length in A.U. at -195° C.	Shift in cm. <sup>-1</sup> from 6934. R <sub>1</sub>	Assignments from the Lattice spectrum in cm. <sup>-1</sup>
6595	6586	761	741 - ν <sub>3</sub>
..	6620	683	..
6649	6640	638	..
6693	6688	530	..
..	6707	488	..
6758	6744	407	412 - ν <sub>2</sub>
6764	6757	378	376 - ν <sub>1</sub>
6817	6807	268	..
7078	7067	273	..
7129	7120	377	376 - ν <sub>1</sub>
7147	7140	416	412 - ν <sub>2</sub>
7188	7178	491	..
..	7196	525	..
..	7260	648	..
7275	7279	683	..
7324	7318	757	741 - ν <sub>3</sub>
	7346	809	847 - ν <sub>4</sub>
	7404	915	909 - ν <sub>5</sub>

image symmetry holds for the bands 6595, 6649, 6693, 6758 and 6817 on the anti-Stokes side and for 7324, 7275, 7188, 7138 and 7078 bands on the Stokes side. It is also possible that besides the principal doublet, the other electronic transitions give rise to vibrational bands in the fluorescence spectrum. This may possibly account for the slight departure from mirror image symmetry about the principal doublet, of the fluorescence and absorption bands observed at liquid air temperature. A more detailed experimental study of the lattice spectrum of alumina is desirable in order to give a complete explanation of the fluorescence and absorption bands exhibited by ruby.

*D. Polarisation Characters.*—Table I indicates that for all bands except 6595, 6693, 6927 and 6942 of ruby, absorption of light takes place almost exclusively in the ordinary spectrum *i.e.*, in the (0001) plane perpendicular to the optic axis of ruby. This absorption, however, has little effect on the emission spectrum, as may be inferred from Figs. 3, 4, 5, 6, 7 and 8 in which the fluorescence bands come out strongly when the electric vector vibrates perpendicular to the optic axis. Therefore, to a first approximation we are justified in ignoring the effect of absorption on the relative intensities of emission bands in polarised excitation. The principal doublet is strongly polarised, the degree of polarisation of 6942 band being higher than that of the 6927 band. Two other electronic bands *viz.*, 6822 and 7049 A.U. are also polarised to the same extent as the latter while the 7016 A.U. band is depolarised. The continuous spectrum is also polarised to the same extent

and in the same sense as the principal doublet. These polarisation characters of the electronic bands support the suggestion that the  $\text{Cr}_2\text{O}_3$  activator possesses a preferred orientation of distribution in the ground lattice. The origin of the polarisation of the electronic bands is not well understood. However, in the present investigation it is observed that the fluorescent vibrations appear stronger with the light vector vibrating normal to the optic axis than when along it, whatever be the nature of the polarisation of the incident light vector. This indicates that the phosphorescent centre in ruby is not a simple electric dipole.

From the values of intensities given in Table III, the vibrational bands have been divided into the following groups, and are listed in Table V.

(1) Bands whose polarisation is in the same sense, and equal to or greater than that of the principal doublet.

(2) Bands whose polarisation is opposite to that of  $R_1$  and  $R_2$  *i.e.*, when the vertical component of the latter is more intense than the horizontal component, the horizontal components of the bands are more intense than the vertical and *vice versa*.

TABLE V

Bands polarised in the same sense as $R_1$ and $R_2$	Bands polarised in the opposite sense to $R_1$ and $R_2$	Bands completely depolarised
I	II	III
6595 ..... $-v_3$		6758 ..... $-v_1$
6693 .....		7129 ..... $+v_1$
7078 .....		7275 .....
7147 ..... $+v_2$		
7188 .....		
7324 ..... $+v_3$	7520 .....	
7725 .....		
7924 .....		

(3) Bands which are completely depolarised, *i.e.*, the vertical and horizontal components are nearly equal in all settings.

It will be seen from the above table that the Stokes and anti-Stokes components of the vibrational bands show more or less the same polarisation characters in polarised excitation. It may also be seen that the two components of the doublet at 7138 are polarised differently, the 7129 component being depolarised nearly to the same extent as the 6758 band on the

anti-Stokes side, while the component at 7147 A.U., having a frequency shift of  $412 \text{ cm.}^{-1}$  appears to be more highly polarised. It is obvious that the vibrations which appear polarised in light scattering should give rise to fluorescence bands which are highly polarised, especially as the principal doublet itself is polarised. This agrees with the assignment of the Raman line at  $412 \text{ cm.}^{-1}$  to the symmetric oscillation. The bands which are completely depolarised and those whose polarisation characters are opposed to that of the principal doublet may be attributed to the degenerate vibrations of the crystal lattice.

In conclusion, the author wishes to express her grateful thanks to Sir C. V. Raman, F.R.S., N.L., for the continued interest he has shown throughout the course of this investigation. My sincere thanks are due to Dr. C. S. Venkateswaran for the valuable help rendered by him.

### *Summary*

The paper deals with the results of a spectroscopic investigation of the fluorescence, absorption and scattering of light in ruby. The first order lattice spectrum of alumina is shown to possess eighteen normal modes of vibrations. Two Raman lines having frequency shifts of 376 and  $412 \text{ cm.}^{-1}$  have been obtained with a single crystal of alumina. The fluorescence and absorption spectra of ruby have been recorded using specially sensitized infra-red plates to register the bands in the long wavelength region with good intensity. The polarisation characters of the bands have also been studied with reference to the direction of the optic axis of the crystal and the direction of polarisation of the incident beam. From a perusal of the results, the emission bands have been divided into two groups *viz.*, (1) electronic bands caused by transitions of the shielded electrons of  $\text{Cr}^{+++}$  ion, (2) vibrational bands arising from a modulation of the electronic transitions by the crystal lattice vibrations. The frequency shifts of eight of the vibrational bands from the principal doublets agree fairly well with one or the other of the observed Raman and infra-red frequencies of alumina. The polarisation characters of the bands on the Stokes sides are also in good agreement with those of the corresponding bands on the anti-Stokes side.

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*Note.*—After the paper had been written, a note by Thosar in the *Physical Review* for October 15, 1941, came to hand which deals with the same subject.