THE INFRA-RED ABSORPTION SPECTRUM OF SILICON CARBIDE

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1. INTRODUCTION

THE earliest investigation of the infra-red behaviour of silicon carbide (carborundum) was carried out by Coblentz[1] who studied the reflexion spectrum in the range $1\,\mu$ to $15\,\mu$ using a large hexagonal plate with natural polish. The remarkably strong reflexion maximum at $12\,\mu$ is the most notable feature of this work. Coblentz also studied the transmission of silicon carbide, but the specimen was opaque beyond $4\,\mu$.

Schæfer and Thomas[2] also studied the reflexion and transmission of silicon carbide between $1\,\mu$ and $15\,\mu$. Their reflexion studies confirm Coblentz's results. Using a very clear uniaxial plate of thickness $0\cdot48$ mm., they were able to investigate the transmission spectrum upto $7\,\mu$. They observed an absorption maximum at $6\cdot24\,\mu$.

In the present paper it is proposed to present the experimental results of the study of the transmission spectra of twelve specimens of silicon carbide from $1\,\mu$ to $20\,\mu$ and discuss them in the light of the X-ray structure determinations.

2. EXPERIMENTAL RESULTS

A Beckman infra-red spectro-photometer (model IR2), provided with potassium bromide optics, was used, the % transmission being read off directly with the instrument. All the specimens are uniaxial and they were studied with their basal plane perpendicular to the infra-red radiation.

Silicon carbide is highly refracting ($\omega = 2\cdot65$, $\epsilon = 2\cdot69$). The incident radiation is, therefore, completely deflected if the plates are not plane parallel. Thus a false absorption is recorded. Out of the twelve specimens examined, three suffered from this defect and did not, therefore, give any useful results. In Figs. 1 to 4 the % cut-off with wavelength are exhibited for specimens I, IX, III and VI respectively.

571

Fig. 1 (Specimen I: thickness 0·14 mm.; transparent and colourless). The % cut-off increases from 60% at 1 μ to 97% at 6·3 μ. There are inflexions in between at 3·5 μ, and at 5 μ. There is a well-defined absorption maximum between 6·3 μ and 6·5 μ. Absorption maxima are also clearly noticed at 7·2 μ and 7·7 μ. The region between 9 μ to 14 μ is a region of almost total absorption. Beyond 14 μ the absorption falls off slowly from 100% to 90%. There are some indications of absorption maxima in this region.

Fig. 2 (Specimen IX: thickness 1 mm.; transparent, slight brown tinge. This shows a general similarity with Fig. 1. But there are absorption maxima at 3·2 μ, 4·5 μ and 5 μ quite easily recognisable. In addition, there are maxima at 6·1 μ, 6·4 μ and 7·3 μ. The region between 9 μ to 15 μ is of almost total absorption. Beyond 15 μ the absorption falls off slowly; the fall is even slower than that noticed in Fig. 1.

Fig. 3 (Specimen VI: thickness = 0·5 mm.; transparent, colourless).

This specimen, besides showing maxima between 6·0 μ and 6·5 μ, and at 7·3 μ, has absorption maxima at 3·2 μ and 5·0 μ. The range between 9·0 μ to 12 μ is one of the intense absorption, after which the absorption falls off very rapidly indeed. In this region there are definite signs of further absorption bands.

Fig. 4 (Specimen III: thickness 0·25 mm., transparent, colourless).

This specimen exhibits inflexions at 3·2 μ, 5·0 μ; well-defined absorption maxima at 6·3 μ, and 7·8 μ; and a region of intense absorption maxima between 10 μ and 13 μ beyond which as in the case of specimen IV, Fig. 3, it shows a rapid fall.

Specimen VIII (curve not reproduced), which is coloured green, is remarkable in that it gives a high transmission (50%) upto 3·0 μ and shows intense and uniform absorption beyond that. Specimens VII and X also behave similarly. All these crystals are green coloured and the above behaviour is presumably due to the colour. Specimen XI (curve not reproduced), shows 50% absorption at 1 μ and gradually goes upto 95% at 6·5 μ where there is a definite absorption band. Beyond 9 μ it shows constant and continuous absorption and falls off slowly beyond 14 μ.

3. CRYSTAL STRUCTURE OF SILICON CARBIDE

Recent work[3] on the X-ray structure of silicon carbide has revealed the existence of numerous modifications. Ramsdell and Kohn list fourteen different silicon carbide structures, viz., one cubic (T_d^2), three hexagonal (C_{6v}^4) and ten rhombohedral (C_{3v}^5, C_{3v}^1).
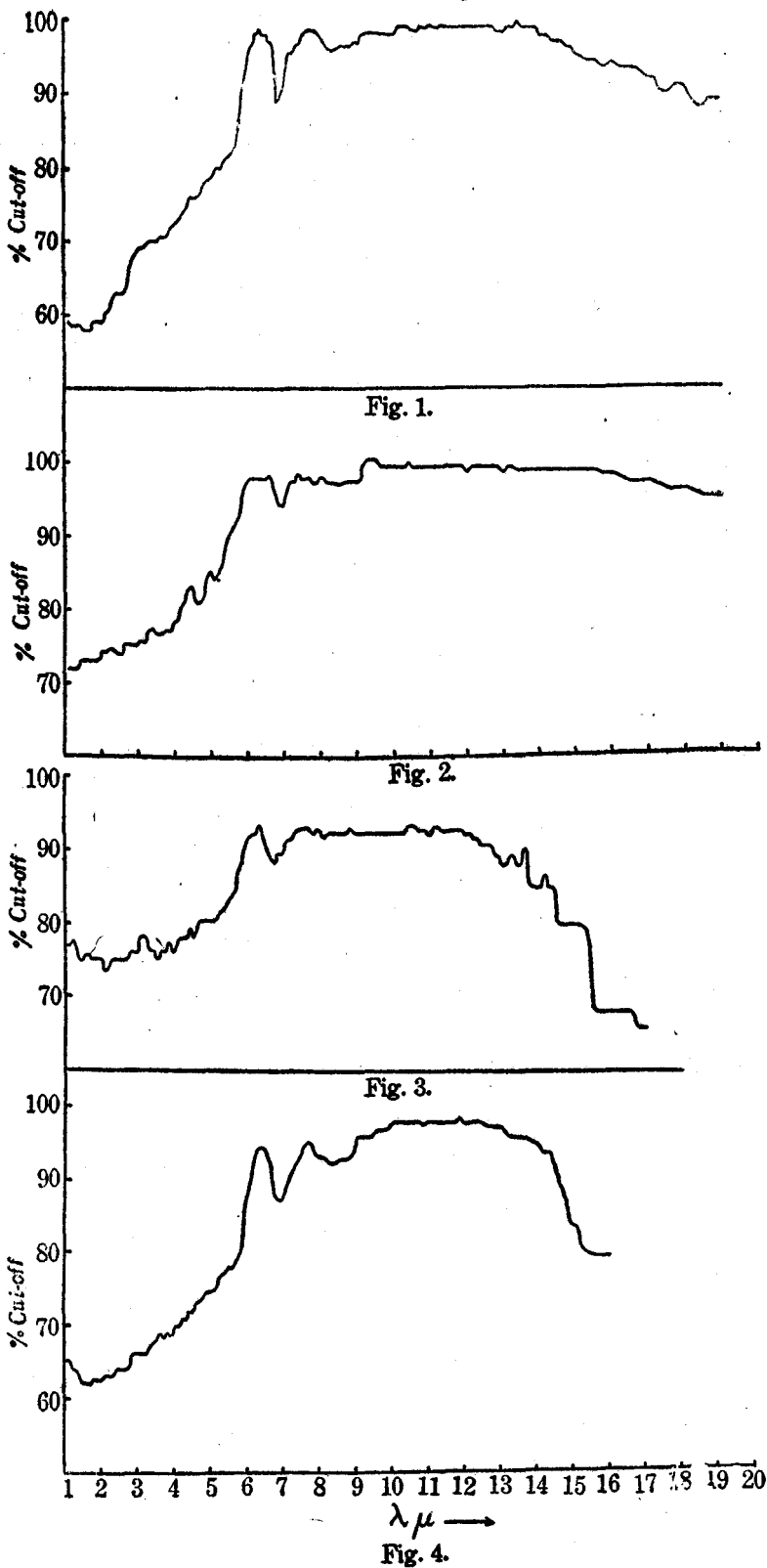
FIGS. 1-4.   Infra-red absorption spectrum of silicon carbide
(Fig. 1 = Specimen I.   Fig. 2 = Specimen IX.   Fig. 3 = Specimen VI.   Fig. 4 = Specimen III)

The crystal forms of silicon carbide, though formally complex, are simple in basic principle. All of them exhibit tetrahedral structure, *i.e.*, each carbon is bound tetrahedrally to four silicons and each silicon to four carbons. The different forms of silicon carbide can be viewed as centres of tetrahedra stacked one above the other in different sheets, the trigonal axis being perpendicular to these sheets. The several structures then differ in the ways in which these tetrahedra are turned with respect to each other.

In the present case as well as in the previous work, the type to which the different specimens belong has not been ascertained. The only fact known is that all of them are uniaxial. But the close relationship between the different forms enables one to interpret the vibration spectrum in a general way.

4. GROUP THEORETICAL ANALYSIS

If the space group and the position and number of atoms in the unit cell are known, the number of normal modes, their symmetry types, and the selection rules governing their infra-red and Raman activity can be deduced from group theoretical analysis.

We shall now apply group analysis to some of the simpler structures.

(i) Type IV, Cubic — SiC — T_d^2.

The unit cell contains two non-equivalent atoms per unit cell [one Si (1) and one C (2)].

T_d^2		E	8 C_3	3 C_2	6σ_d	6 S_4	n_i	T	n_i'	R	I.R.
A_1	..	1	1	1	1	1	0	0	0	—	—
A_2	..	1	1	1	−1	−1	0	0	0	—	—
E	..	2	−1	2	0	0	0	0	0	—	—
F_2	..	3	0	−1	1	−1	2	1	1	a	a
F_1	..	3	0	−1	−1	1	0	0	0	—	—
U_R	..	2	2	2	2	2					

Thus this structure is capable of a triply degenerate vibration, active both in Raman effect and infra-red. In vibration the silicons vibrate against carbons in any arbitrary direction. The normal co-ordinates are:

$$Q_a = m_{si}x_2 - m_c x_1 \text{ and similarly } Q_b, \text{ and } Q_c.$$

(ii) Type III, 4H, Hexagonal: C_{6v}^4, four SiC per unit cell,

(1 to 4 silicons, 5 to 8 carbons)

$C_{6v}{}^4$		E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$	n_i	T	$n_i{}'$	R	I.R.
A_1	..	1	1	1	1	1	1	4	1	3	a	a
A_2	..	1	1	1	1	−1	−1	0	0	0	−	−
B_2	..	1	−1	1	−1	1	−1	0	0	0	−	−
B_1	..	1	−1	1	−1	−1	1	4	0	4	ia	ia
E_2	..	2	2	−1	−1	0	0	4	0	4	a	ia
E_1	..	2	−2	−1	1	0	0	4	1	3	a	a
U_R	..	8	0	8	0	0	8					

The form of the normal co-ordinates is:

$$\underline{A_1} \rightarrow Q_i = c_1 (z_1 + z_2) + c_2 (z_3 + z_4) + c_3 (z_5 + z_6) + c_4 (z_7 + z_8)$$
$$(i = 1, 2, 3, \text{ or } 4)$$

As one translation belongs to this class, one of the normal co-ordinates is:

$$T_z = z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8.$$

$$\underline{B_1} \rightarrow Q_i = c_1 (z_1 - z_2) + c_2 (z_3 - z_4) + c_3 (z_5 - z_6) + c_4 (z_7 - z_8).$$

$$\underline{E_1} \rightarrow Q_{ia} = a_1 (x_1 + x_2) + a_2 (x_3 + x_4) + a_3 (x_5 + x_6) + a_4 (x_7 + x_8)$$

and similarly Q_{ib}. Of these

$$Tx = x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8$$
$$Ty = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8.$$

$$\underline{E_2} \rightarrow Q_{ia} = b_1 (y_1 - y_2) + b_2 (y_3 - y_4) + b_3 (y_5 - y_6) + b_4 (y_7 - y_8)$$

and similarly Q_{ib}.

For the type-6H also one may similarly apply the same method. The number of normal modes in this type naturally increases for each symmetry class, though the general nature of the movements is the same. We thus find that in the hexagonal types of silicon carbide the movements of the atoms are either along the trigonal axis or perpendicular to it.

(iii) Type I, 15 R − SiC. Rhombohedral.—$C_{3v}{}^5$.

Five SiC per unit cell (1 to 5 Si; 6 to 10 C).

$C_{3v}{}^5$		E	$2C_3$	$3\sigma_v$		n_i	T	$n_i{}'$		R	I.R.
A_1	$\cdot\cdot$	1	1	1		10	1	9		a	a
A_2	$\cdot\cdot$	1	1	-1		0	0	0		ia	ia
E	$\cdot\cdot$	2	-1	0		10	1	9		a	a
U_R	$\cdot\cdot$	10	10	10							

The form of the normal co-ordinates is:

$$A_1 \rightarrow Q_i = \overset{10}{\underset{1}{\Sigma}}\, c_i z_i, \quad T_z = \overset{10}{\underset{1}{\Sigma}}\, z_i$$

$$E \rightarrow Q_{ia} = \overset{10}{\underset{1}{\Sigma}}\, a_i x_i, \quad T_x = \overset{10}{\underset{1}{\Sigma}}\, x_i$$

and similarly Q_{ib}.

In this type the oscillations are again confined to the direction along the trigonal axis or perpendicular to it.

5. Interpretation of Observed Facts

From the above analysis it emerges that the normal modes of all the structures of silicon carbide consist of movements of layers perpendicular to the trigonal axis. The movements are either normal to the axis or along it. In the cubic silicon carbide, there is only one normal mode in which silicons oscillate against carbons. In all types of silicon carbide there will be a mode in which silicons and carbons vibrate in opposite phases. This type of oscillation will have the highest frequency and will be active in both infra-red and Raman effect.

The Raman spectrum of specimen IX has been examined by Narayanan.[4] He obtained a line at 818 cm.$^{-1}$ (12·2 μ). The reflexion studies also indicate an extremely intense maximum at 12 μ, while all crystals studied in this investigation show an intense absorption in the range 10 μ to 14 μ. The calculation of the frequency of the only normal mode of the cubic carborundum, making certain assumptions about the force constants (by comparison with the analogous case of diamond), suggests qualitatively that the principal oscillation in which carbons vibrate against silicons, can be ascribed to this 12 μ band, active both in infra-red and Raman effect.

The absorption spectra as well as the group theoretical analysis, however, clearly indicate the existence of numerous other vibrations than the one described above. These will be of lower frequencies and their number will increase with the increasing complexity of the structure. The vibrations

which will be active in infra-red when the crystals are examined in the basal plane, are those in which movements are normal to the optic axis. Even in the simplest type (4H) there are two such vibrations besides the one in which carbons vibrate against silicons. This no doubt accounts for the intense absorption which continues beyond 12μ.

The absorption maxima at $3 \cdot 5 \mu$, $5 \cdot 0 \mu$; $6 \cdot 3 \mu$ to $6 \cdot 5 \mu$; and at $7 \cdot 2 \mu$ and $7 \cdot 7 \mu$ in specimen I; $3 \cdot 2 \mu$, $4 \cdot 5 \mu$, $5 \cdot 0 \mu$, $6 \cdot 1 \mu$, $6 \cdot 4 \mu$ and $7 \cdot 3 \mu$ in specimen IX; $3 \cdot 2 \mu$, $5 \cdot 0 \mu$; $6 \cdot 0 \mu$ to $6 \cdot 5 \mu$ in specimen VI; $3 \cdot 2 \mu$, $5 \cdot 0 \mu$, $6 \cdot 3 \mu$ and $7 \cdot 8 \mu$ in specimen III—all these can be interpreted as first order and second order combinations and overtones of the fundamentals. This also indicates the existence of fundamentals other than the one at 12μ.

In conclusion, I wish to express my grateful thanks to Professor Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for his encouragement and guidance.

SUMMARY

The absorption spectra of crystals of silicon carbide, studied in the range of 1μ to 20μ, reveal besides an intense region of absorption from 10μ to 14μ in which the reflexion maximum at 12μ falls, several comparatively well-defined absorption maxima at shorter wavelengths, *viz.*, at $3 \cdot 5 \mu$, $5 \cdot 0 \mu$, $6 \cdot 3 \mu$ to $6 \cdot 5 \mu$, $7 \cdot 2 \mu$ and $7 \cdot 7 \mu$ in a typical case.

Silicon carbide exists in various crystal forms. From a group theoretical analysis applied to a few typical cases it emerges that the normal modes of the uniaxial silicon carbide consist of movements of silicons and carbons along the optic axis or normal to it.

The reflexion maximum at 12μ, and the Raman line at $818 \mathrm{~cm.}^{-1}$ ($12 \cdot 2 \mu$) can be attributed to an oscillation in which carbons and silicons vibrate in opposite phases. The existence of numerous other vibrations besides this one accounts for the extension of the absorption band beyond 12μ. The absorption maxima in the short wavelengths can be attributed to first order and second order combinations and overtones of these fundamentals.

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