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THE NEAR INFRA-RED ABSORPTION SPECTRA OF CALCITE AND STRONTIANITE

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ABSTRACT

A study of the near infra-red absorption spectra of calcite and strontianite has been made by using thick specimens. With a specimen 2 cm thick, cut at right angles to the optic axis, bands were observed for calcite at 1.76μ, 1.90μ, 2.00μ and 2.20μ. These bands have the same characteristics as those observed by Schaefer, Bermuth and Matossi in the near infra-red. The second order equations have been applied to the bands observed in this work and to those observed by Schaefer and it was found that series relationships existed between them with only small deviations of the observed from the calculated values. In strontianite a similar set of bands was observed at 1.89μ, 2.01μ and 2.19μ, and they were of the same type as those for calcite. The value of the inactive fundamental was calculated and found to correspond to a band at 9.2μ, which is in good agreement with the value of 8.98μ found theoretically by Nielsen.

INTRODUCTION

THE infra-red absorption spectra of several carbonates in crystal form have been measured by different observers.[1,2] Moreover, Schaefer and Schubert[3] have found regions of intense selective reflection at 6.7μ, 11.38μ and 14.16μ in the reflection spectra of calcite which they attributed to the fundamental vibrations of the carbonate ion. The band at 11.38μ was found to be due to a vibration along the optic axis and the bands at 6.7μ and 11.38μ were found to be due to vibrations at right angles to the optic axis. The absorption measurements of Schaefer, Bermuth and Matossi included the region from 2μ to 20μ and it was found that the spectra of the different carbonates studied had almost similar bands, from the standpoint of intensity and location, in the region from 2μ to 7μ. The bands in this region were attributed to the harmonics and the combinations of the fundamental vibrations of the carbonate ion.

From theoretical considerations Kornfeld[4] has shown that the carbonate ion should have three active and one inactive vibration, the inactive vibration corresponding to a band at about 8μ. Certain bands were found which were attributed to a combination including this inactive vibration but fairly large differences were found between the theoretical and calculated values. More recently Nielsen[5] has considered the vibrations of the carbonate ion from a point of view somewhat different from Kornfeld's and has

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[1] Schaefer, Bermuth and Matossi, Zeits. f. Physik **39**, 648 (1926).

[2] Rawlins and Rideal, Proc. Roy. Soc. **A116**, 140 (1927).

[3] Schaefer and Schubert, Ann. d. Physik **50**, 283 (1916).

[4] Kornfeld, Zeits. f. Physik **26**, 205 (1924).

[5] Nielsen, Phys. Rev. **32**, 773 (1928).

obtained a value of about 9μ for the inactive fundamental which is in good agreement with the value obtained from observations of Schaefer.

The present work was undertaken in order to extend the bands of the carbonates into the near infra-red and to test the series relationships for this region.

Experimental Procedure

A clear section of calcite 2 cm thick was cut at right angles to the optic axis and was then placed in and out of a beam of radiation so that the relative transmission could be determined for each setting of the prism. A Hilger infra-red spectrometer with a quartz prism was used as the resolving instrument. The instrument was calibrated by means of certain lines and bands in the near infra-red which had been measured by other observers. A steady and intense source of radiation was obtained by sending a current of three amperes from a set of storage batteries through a piece of globar. The detecting system consisted of a linear thermopile connected in series with a low resistance galvanometer having sensitivity of 10 mm per microvolt. The thermopile slit included about 0.02μ in the region of 2μ. The telescope and scale were two meters from the galvanometer, the average deflection was 15 cm, and each deflection was estimated to 0.02 cm. When the crystal was in the beam of radiation, the deflections were never smaller than 2 cm. In measuring the absorption of strontianite in the region from 1.5 to 2.5μ a section 6 mm thick cut perpendicular to the optic axis was used.

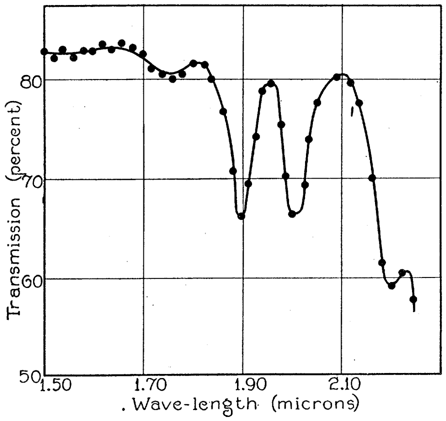

Fig. 1. The absorption spectra of calcite for a section 2 cm thick cut perpendicular to the optic axis.

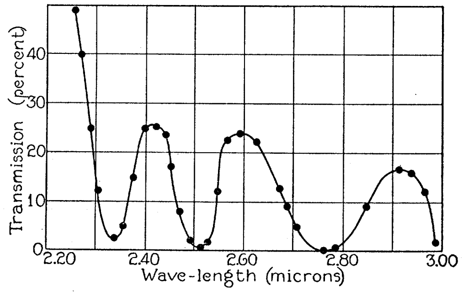

Fig. 2. The absorption spectra of calcite from 2.2μ to 2μ.

Results

The absorption spectrum for calcite in the region from 1.70μ to 2.64μ is shown in Fig. 1 and in Fig. 2. The bands at 2.34μ and 2.52μ were observed by Schaefer, Bermuth and Matossi, but those at 1.76μ, 1.90μ, 2.00μ and 2.20μ have not been previously reported. The region from 1.20μ to

1.50μ was also studied but no bands were found. In Fig. 3 the absorption bands of strontianite are shown. These are weaker and the transmission between the bands is not as large as for calcite. There were several cleavage fractures in the specimen and this probably caused the transmission to be less. Also, since the thickness of the crystal was 6 mm as compared with 2 cm for the calcite, a set of bands of less intensity might have been expected.

It has already been stated that all the observed bands for carbonates in the near infra-red are due to vibrations of the carbonate ion. The more intense of these may be identified with the harmonics of the band at about 6.7μ, called ν_1, or with combinations of ν_1 with ν_0, and ν_2 (ν_2 being used to denote the band at 13.78μ and ν_0 the inactive frequency corresponding to a band at 9μ). The three intense bands between the region ν_1 and $2\nu_1$ have been identified with the combinations $\nu_2+\nu_0$, $\nu_1+\nu_2$ and $\nu_1+\nu_0$ by Schaefer, Bermuth and Matossi[1] while those between $2\nu_1$ and $3\nu_1$, correspond to the combinations $\nu_1+\nu_2+\nu_0$, $2\nu_1+\nu_2$ and $2\nu_1+\nu_0$. The bands observed by the writer may be identified with the combinations $2\nu_1+\nu_2+\nu_0$, $3\nu_1+\nu_2$ and $3\nu_1+\nu_0$. Table I gives the observed and calculated positions of the bands together with their identification. The experimental values marked with an asterisk are those which have been found by the present investigation, the remainder for calcite are taken from the work of Schaefer. The calculated values differ from those of Schaefer because the values for ν_2 have been calculated from absorption rather than reflection and because the value of ν_1 has been determined by applying the second order equations to the observed frequencies of the harmonics. In the calculations only the more intense component of a complex band was considered. The bands of strontianite at 1.89μ, 2.01μ and

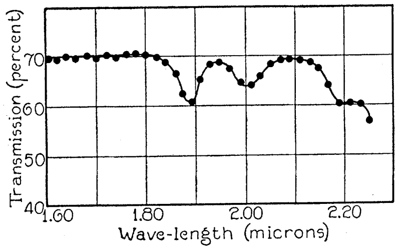

Fig. 3. The absorption spectra of strontianite for a section 6 mm thick.

TABLE I. *Observed and calculated bands of calcite and strontianite.*

Calcite			Strontianite	
Obs.	Cal.	Combination	Obs.	Cal.
1.76μ*	1.77μ	$4\nu_1$		1.80
1.90*	1.87	$3\nu_1+\nu_0$	1.89μ*	1.88
2.00*	2.00	$3\nu_1+\nu_2$	2.01*	2.02
2.20*	2.16	$2\nu_1+\nu_2+\nu_0$	2.19*	2.15
2.34*	2.33	$3\nu_1$	2.34	2.34
2.52*	2.53	$2\nu_1+\nu_0$	2.55	2.53
2.77*	2.78	$2\nu_1+\nu_2$	2.82	2.78
3.10	3.10	$\nu_1+\nu_2+\nu_0$	3.10	3.09
3.47	3.50	$2\nu_1$	3.45	3.45
3.92	3.96	$\nu_1+\nu_0$	3.97	3.94
4.64	4.64	$\nu_1+\nu_2$		
5.55	5.52	$\nu_2+\nu_0$		
	6.92	ν_1		6.75
13.92	13.92	ν_2	14.35	14.35
	9.20	ν_0		9.40

* Bands observed in the present work.

2.19μ have been observed in the present work and the other bands to 4μ have been observed by Rawlins and Rideal.[2] The fourth overtone of the intense band at 7μ was not observed. The check between the computed and experimental values is very good and it is found that the divergencies which do appear are not incompatible with the form of the second order correction terms.

It is of interest to note that the calculated value of the inactive frequency gives a value of 9.2μ which is in good agreement with the value of 8.98μ obtained theoretically by Nielsen. Taylor[6] has considered the supposition of an inactive fundamental being active in combination as somewhat artificial. However, this objection does not seem valid in view of the experimental and theoretical evidence, and especially since Wood[7] has recently shown that calcite gives a Raman effect line corresponding to a band at 9.19μ.

The calculated values of the two components of the fundamental at 6.7μ obtained from the observed values of the overtones, give values of 6.42μ and 6.92μ for the two maxima. An experimental study has been made of the reflection spectra of calcite in this region in order to see if these maxima were present. A Hilger infra-red spectrometer with a rock-salt prism was used as the resolving instrument. Four maxima were observed at 6.36μ, 6.54μ, 6.62μ and 7.05μ, the two components at 6.54μ and 7.05μ being much more intense. The reflection spectra are shown in Fig. 4 for this region. The writer[8] had previously noted the existence of these bands and at that time an attempt was made to identify the separate maxima with effects produced by the calcium atom. However, both theory and experiment point to the fact that the 7μ band of the carbonates is due to the carbonate ion and that the above interpretation is untenable. While all the bands observed for the carbonates have not been identified with combinations of the fundamental frequencies, yet the near infra-red bands may be arranged in three series which are found to correspond with simple combinations of the fundamentals.

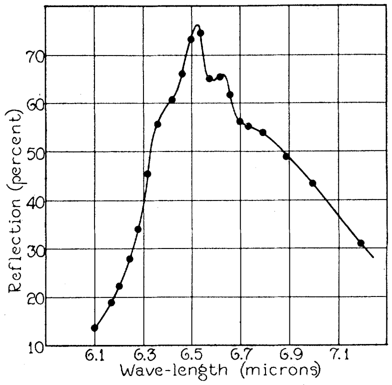

Fig. 4. The reflection spectra of calcite in the region of 7μ.

The writer is indebted to Professor D. M. Dennison for some suggestions made in reference to this work.

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January 30, 1929.

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[6] Taylor, Phil. Mag. **6,** 88 (1928).

[7] Wood, Phil. Mag. **6,** 729 (1928).

[8] Plyler, Science **55,** 578 (1927).