TEMPERATURE VARIATION OF THE RAMAN SPECTRUM OF ANHYDRITE

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Summary

The temperature dependence of the Raman spectrum of anhydrite has been studied over the range of temperature from 90° K. to 670° K., using the λ 2537 resonance radiation of mercury as the exciter. From the measured frequency shifts the $\chi \left(= -\frac{1}{\nu} \cdot d\nu/d\tau\right)$ values have been calculated for the lines 135, 674, 1018, 1127 and 1160 cm.$^{-1}$ The value of χ is different for different Raman lines and for individual Raman lines it increases with temperature.

The temperature variation of the width of the 1160 cm.$^{-1}$ line has also been measured. The intensity of the line 135 cm.$^{-1}$ increases with temperature, whereas the intensities of the lines 500 cm.$^{-1}$, 1127 cm.$^{-1}$ and 1160 cm.$^{-1}$ decrease.

1. Introduction

The Raman spectrum of anhydrite ($CaSO_4$) has previously been investigated in detail by Couture (1948) and Krishnan and Shantakumari (1950). The temperature variation of its Raman spectrum has not been studied so far. As the crystal is capable of withstanding temperatures up to 450° C., its Raman spectrum has been studied over a wide range of temperatures and the results are presented in this paper.

2. Experimental Details

A natural crystal of anhydrite having the dimensions $16 \times 10 \times 6$ mm. with the edges parallel to the *a*, *b*, *c* axes respectively, was used in the present investigation. The technique used for work below room temperature was similar to that used by Krishnan (1947), Narayanaswamy (1947) and others in this laboratory. Liquid air and a mixture of pulverised ice and salt were used as refrigerants and the corresponding temperatures were 90° K. and 258° K. respectively.

To record the spectrum above room temperature, the crystal was kept inside a heater provided with suitable windows. The heating current was drawn from the D.C. mains and was adjusted with the aid of a rheostat. The steady state was reached within 30 minutes after switching on the current. The heater had to be clamped such that light from the intense portion of the quartz mercury arc was incident along the *c*-axis of the crystal and the scattered light was observed along the *b*-axis.

The temperature of the crystal was measured by an iron-constantan thermocouple whose junction was kept close to the crystal. To measure the thermo E.M.F. a calibrated microammeter was used. The spectra were photographed with the crystal maintained consecutively at the following temperatures: 90, 258, 298, 371, 403, 433, 463, 516, 593 and 673° K. Using a medium quartz spectrograph and a slit width of ·02 mm., exposures of the order of 12 hours were given to get fairly intense spectrograms. In order to measure the frequency shifts accurately, a comparison iron arc spectrum was superimposed on each Raman spectrum.

3. RESULTS

The observed frequency shifts of the Raman lines of anhydrite at room temperature agree well with those reported by Krishnan and Shantakumari (1950). The spectra photographed using a Hartmann diaphragm with the crystal maintained at the temperatures 317° K. and 673° K. are reproduced in Fig. 1 on Plate VIII. As some of the intense Raman lines (415, 608, 628, 1018 cm.$^{-1}$) were adjacent to the fairly intense mercury lines, their shifts with temperature could not be measured accurately. The lines 415 cm.$^{-1}$ and 500 cm.$^{-1}$ (recorded on the anti-Stokes side also) do not show any appreciable variation in frequency shift. The values of the change in frequency shifts of the Raman lines 1127 cm.$^{-1}$ and 1160 cm.$^{-1}$ for different temperatures are given in Table I. The width at half intensity of the line

TABLE I

Temperature variation of the frequency shifts of two prominent Raman lines of anhydrite

Temperature °K.	1127 cm.$^{-1}$		1160 cm.$^{-1}$		
	Position cm.$^{-1}$	Shift cm.$^{-1}$	Position cm.$^{-1}$	Shift cm.$^{-1}$	Width cm.$^{-1}$
90	1130·0	2·6	1163·6	3·6	..
258	1128·3	0·9	1161·0	1·0	..
298	1127·4	0	1160·0	0	7·8
371	1125·7	— 1·7	1158·1	— 1·9	8·6
403	1124·8	— 2·6	1157·1	— 2·9	9·0
433	1123·6	— 3·8	1156·3	— 3·7	9·6
463	1123·1	— 4·3	1155·5	— 4·7	10
516	1120·8	— 6·6	1153·5	— 6·5	10·9
593	1118·6	— 8·8	1151·1	— 8·9	13
673	1114·6	—12·8	1147·4	—12·6	15·6

1160 cm.$^{-1}$ was estimated from the microphotometer record and the values at different temperatures from 298° K. to 673° K. are also included in Table I (last column). As the slit width and the crystal orientation used for photographing the Raman spectra at 90° K. and 258° K. were different from those used at the other temperatures, the widths of the line at these two temperatures are not included in the table.

From the measured frequency shifts, the values of $\chi (= -1/\nu \cdot d\nu/d\tau)$ for five Raman lines have been calculated for the two temperature ranges from 90° K. to 298° K. and from 298° K to 673° K. They are entered in Table II together with the shifts for the respective ranges.

TABLE II

Total shift and the value of χ for various Raman frequencies of anhydrite

Raman frequency cm.$^{-1}$	From 90° K. to 298° K.		From 298° K. to 673° K.	
	Shift cm.$^{-1}$	$\chi \times 10^6$	Shift cm.$^{-1}$	$\chi \times 10^6$
135	5·2	185	9·8	194
674	1·1	7	6·9	29
1018	1·1	5	9·3	26
1127	2·6	11	12·8	30
1160	3·6	15	12·6	29

4. DISCUSSION

From a study of Table II it is evident that the expression $\chi (= -1/\nu \cdot d\nu/d\tau)$ is different from different Raman frequencies. Also, for individual Raman lines it varies with temperature.

The width of the Raman lines, attributable to the thermal fluctuations in density inside the crystal, is also appreciably influenced by temperature. As the temperature is increased some of the Raman lines become broader and spread over a finite range of wave numbers. There is a striking similarity between the temperature-frequency shift and the temperature-width variations. In both cases the rate of change is higher at higher temperatures. Such a similarity has been observed previously in the case of calcite and quartz by Narayanaswamy (1947) and $NaClO_3$ and $KClO_3$ by Shantakumari (1950).

The intensities of the Raman lines are also affected by temperature. The aggregate intensity of the '135' line increases with increase of temperature, whereas the intensities of the lines 500 cm.$^{-1}$, 1127 cm.$^{-1}$ and 1160 cm.$^{-1}$ decrease.

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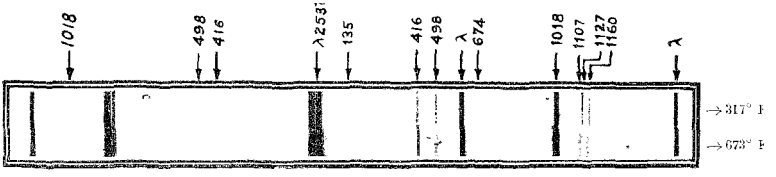

FIG. 1. Raman Spectrum of anhydrite at two different temperatures