RAMAN SPECTRUM OF FLUORSPAR AND ITS TEMPERATURE VARIATION

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1. INTRODUCTION

Fluorspar crystallises in the cubic system, the space group being \( O_\overline{4} \). The structure is made up of three interpenetrating face-centred lattices two of which are of fluorine atoms and the third of calcium atoms. It can be considered as a unit cube of calcium atoms in which the fluorines are situated at the body centres of eight small cubes formed by joining the mid-points of the edges of the unit cube. Every calcium atom is surrounded by eight fluorines and every fluorine by four calciums.

As specimens of fluorspar were readily available, it was one of the solids with which the earliest attempts to record a Raman spectrum was made. Nisi (1929) tried to obtain the Raman spectrum of fluorspar using \( \lambda 4358 \) radiation of the mercury arc as exciter, but failed to get any effect. A little later, the employment of a more powerful technique of excitation, namely the use of the \( \lambda 2536 \) resonance radiation enabled Rasetti (1931) to successfully record the spectrum of fluorspar. It exhibited a single line with a frequency shift \( 321.5 \text{ cm}^{-1} \). This frequency represents the fundamental vibration of the fluorspar structure, \textit{viz.}, the mode in which the two fluorine lattices oscillate against each other, the calcium lattice being at rest. This mode, according to the usual selection rules, should be active in the Raman effect. Rasetti, however, identified the observed Raman shift with the reststrahlen frequency of fluorspar appearing at \( 31 \mu \).

The author has re-examined the Raman spectrum of fluorspar using the Rasetti technique and has confirmed the appearance of the Raman line at \( 321.5 \text{ cm}^{-1} \). Using a crystal of calcium fluoride of size \( 2.5 \times 2.5 \times 2.5 \) cm. and the medium quartz spectrograph, exposures of about six days failed to record any Raman line other than the one at \( 321.5 \text{ cm}^{-1} \).

2. WORK AT HIGH TEMPERATURES

In order to study the temperature variation of the Raman frequency of fluorspar, a crystal of fluorspar in the form of a polished plate \( 2.5 \text{ cm} \),
A casing of brass 3.0 cm. × 2.5 cm. × 1.1 cm. was made for holding the crystal. A rectangular aperture measuring 1.0 cm. × 0.8 cm. was made in one of the sides of the casing for the purpose of illuminating the crystal. The whole of the outside of this casing except for the window was covered with a thin sheet of mica and was then closely wound with strip heating wire. A coating of alumina mixed in sodium silicate was applied over the windings for the purpose of insulating them. When this coating had dried, a plane-parallel fused quartz plate was fixed on the window and the furnace was then wrapped with an aluminium foil in order to reduce loss of heat by radiation. A slit measuring 0.15 cm. × 1.0 cm. was made in the middle of the front end of the casing. The junction of an iron-constantan thermocouple was placed in direct contact with the crystal but thermally insulated from the inside surface of the metal casing. The furnace was fed by a battery of accumulators, the current being adjusted by a rheostat. It was necessary to prepare a schedule of the maximum steady temperatures attained with various known currents through the heating coil of the furnace with the crystal in position. This was accordingly done in a preliminary experiment. The light scattered by the crystal was focussed on the slit of the spectrograph by means of a quartz lens. The slit width used was 0.02 mm. and all the exposures were of three hours duration. The spectra were recorded on Ilford Selochrome plates and each spectrum was accompanied by an iron-arc spectrum superposed on it at its centre for comparison. During an exposure the temperature of the crystal was maintained constant by adjusting the current through the furnace. At low temperatures the furnace maintained a fairly steady temperature, but frequent adjustments were necessary at higher temperatures. The negatives were finally measured under a Hilger cross-slide micrometer and the frequency shift of the observed Raman line was calculated. To measure the width of the Raman line at different temperatures, the spectrograms were micro-photometered. From the micro-photometer records, the width of the line at half intensity was estimated.

3. RESULTS

Fig. 1 (a) on Plate I is a reproduction of the Raman spectrum of fluorspar taken with the large El quartz spectrograph. The spectrum exhibits only a single intense Raman line. The most interesting feature is the extraordinary breadth of this line. This was not pointed out by Rasetti. The frequency shift and width of the line at 40° C. as measured from this spectrogram are 321.5 cm.⁻¹ and 8.7 cm.⁻¹ respectively. The value obtained by Rasetti for the frequency shift is 321.5 cm.⁻¹.
TABLE I. Temperature Variations of the Raman Line of Fluorspar

<table>
<thead>
<tr>
<th>Temperature $°K$</th>
<th>Position</th>
<th>Shift cm.$^{-1}$</th>
<th>Width at half intensity cm.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>321.5</td>
<td>0</td>
<td>8.7</td>
</tr>
<tr>
<td>317.5</td>
<td>321.3</td>
<td>0.2</td>
<td>8.7</td>
</tr>
<tr>
<td>345.8</td>
<td>319.3</td>
<td>2.2</td>
<td>10.0</td>
</tr>
<tr>
<td>402.5</td>
<td>317.4</td>
<td>4.1</td>
<td>12.7</td>
</tr>
<tr>
<td>465.8</td>
<td>315.0</td>
<td>6.5</td>
<td>14.9</td>
</tr>
<tr>
<td>494.7</td>
<td>313.7</td>
<td>7.8</td>
<td>16.9</td>
</tr>
<tr>
<td>526.9</td>
<td>312.6</td>
<td>8.9</td>
<td>17.0</td>
</tr>
<tr>
<td>559.5</td>
<td>312.2</td>
<td>9.3</td>
<td>20.8</td>
</tr>
</tbody>
</table>

Figs. I (b), (c) and (d) in Plate I represent the spectrograms taken at 44.5° C., 161.3° C. and 286.5° C. The measured variations in position and breadth of the Raman line are given in Table I. The line has an appreciable width even at room temperature. As the temperature is raised, the frequency shift of the line diminishes and the width increases, the increase in width being of the same order of magnitude as the displacement in its frequency shift. The temperature variations in the frequency shift and width of the line are graphically represented in Fig. 2. It is seen from the figure that the temperature-width and the temperature-frequency shift

![Graph showing temperature dependence of frequency shift and width of the Raman line of fluor spar](image-url)
Fig. 1. (a) Raman spectrum of fluorspar taken with a E1 quartz spectrograph.

(b), (c) and (d) Raman spectra taken with a medium quartz spectrograph with the crystal kept at 44.5°C, 161.3°C, and 280.5°C.
curves are similar in shape showing thereby that the variations of frequency shift and width of the Raman line with temperature are closely related to each other. Similar observations have already been reported by Narayanaswamy (1947, 1948) for the Raman lines of calcite, quartz and barytes.

The mean proportional change in the frequency, namely \(-\frac{1}{\nu} \frac{dv}{dT}\) which is denoted by \(\chi\) has been evaluated. For the temperature range 313° to 559·5° K., \(\chi\) has a mean value of 118 \times 10^{-6}. This is of the same order of magnitude as the \(\chi\) value for the lattice lines of barytes observed by Narayanaswamy (1948). The relative change of frequency of the Raman line with relative change of volume which is expressed as \(\gamma_v\):—

\[
\gamma_v = -\frac{\Delta \nu}{\nu} \frac{V}{\Delta V} = -\frac{dv}{dT} \cdot \frac{1}{\nu} \frac{1}{3\alpha_L},
\]

where \(\alpha_L\) (coefficient of linear expansion), has also been evaluated, over the temperature range 313° to 559·5° K.

Mean value of \(\gamma_v\) = 1·7.

The value of \(\alpha_L\) was taken from the measurements of the author (D. C. Press, 1949). The mean value of the Gruneisen constant \(\gamma\) is equal to 1·9. Because of the finite width of the Raman line of fluorspar and consequent error in the measurement of \(\Delta \nu\), it is too premature to attach any significance to the difference in the calculated values of \(\gamma_v\) and \(\gamma\).

In conclusion, the author wishes to express his grateful thanks to Sir C. V. Raman for the loan of the fluorspar crystal and also to Prof. R. S. Krishnan for valuable discussions.

**SUMMARY**

Using the \(\lambda 2536\) Hg resonance radiation as exciter, the Raman spectrum of fluorspar has been investigated over the range of temperature from 313° K. to 559° K. The spectrum exhibits a single Raman line with a frequency shift 321.5 cm\(^{-1}\) at 313° K. which decreases to 312.2 cm\(^{-1}\) at 559° K. The width of line increases from 8·7 cm\(^{-1}\) to 20·8 cm\(^{-1}\) over the same range of temperature. The temperature-frequency shift and the temperature-width curves are similar in nature.

**REFERENCES**