EFFECT OF CRYSTAL ORIENTATION ON THE RAMAN SPECTRUM OF BARYTES

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1. Introduction

The detailed study of light scattering in single crystals has assumed considerable importance in recent times on account of its relation to the theory of the solid state. The study which is conducted both with reference to the orientation of the crystal and the state of polarisation of the incident and scattered light is limited by the difficulty of obtaining a single crystal of suitable size with flawless interior and clear surfaces. In the case of barytes (barium sulphate) the natural crystal answers our purpose very well and can be obtained relatively clear and in large sizes. Barytes naturally crystallises in the di-digonal equatorial class of the orthorhombic system. According to the Dana, the Schoenflies and the Groth systems, it falls under the normal, the holohedral and the rhombic bi-pyramidal classes respectively. This crystal group requires as co-ordinate axes three lines of unequal unit lengths perpendicular to one another. The ratio of the crystallographic axes is given by \( a : b : c = 0.8152 : 1 : 1.3136 \). X-ray studies by James and Wood (1925) show that the atomic structure of barytes possesses a unit orthorhombic cell, the dimensions of which correspond, in terms of the crystal ratio to \( 2a, 1b, 1c \), *i.e.*, \( 1.6304 : 1 : 1.3136 \). From the specific gravity and molecular weight of the crystal, we find the unit parallelepiped contains 4 molecules of \( \text{BaSO}_4 \). Of the several forms in which barytes naturally crystallises, though two were available in the collection of Professor Sir C. V. Raman, only crystals having the oblique parallelepiped habit were used in the experiments detailed below.

Despite the abundance and the ease with which crystals of barytes could be secured, it is surprising that very little work has been done on the crystal. It was therefore thought that a detailed study of the scattering in barytes with a view to secure a complete spectrum of the Raman effect would be profitable.
The results that have been obtained and are reported in this paper have justified the investigation.

2. Experimental

The investigation was carried out at room temperature (about 25° C.) with two crystals of the parallelepiped form. Of the two, the smaller crystal measured nearly 7 cm. x 6 cm. x 3 cm. and the larger 8 cm. x 6 cm. x 4 cm. The planes (001), (110) and (110) are perfect cleavage planes in the crystal. Hence the crystal was illuminated in a direction perpendicular to the (110) plane, and the light scattered was observed in directions perpendicular to the (001) and (110) planes. The spectrograms obtained are marked (c) and (a) respectively in Fig. 1 of the Plate. It was then illuminated along the c-axis which is perpendicular to the (001) plane and the scattered light observed perpendicular to the (110) plane, and the spectrogram (b) in the plate was obtained.

The scattering was very weak in the crystal and it was found that exposures extending to over three days were necessary even when the Zeiss three-prism spectrograph with a short camera of focal length 12 cm. was used for securing the spectrograms. Of the three orientations, the scattering in the (b) orientation was fainter than in the other two cases which were nearly equal. This necessitated a longer exposure in the (b) orientation in order to obtain a picture of the same density as in the other two spectrograms.

3. Results

Krishnamurti (1930), Nisi (1931) and Rasetti (1931) have worked with single crystals of barium sulphate. The frequency shifts observed by them along with those of the author, obtained in the three orientations, are tabulated in Table I.

Spectrograms obtained by the use of incident unpolarised light for the three different orientations of the crystal described above are reproduced as Fig. 1 in the Plate. It is found that no particular orientation gives us the complete Raman spectrum of barium sulphate. A perusal of the table shows that fifteen shifts have been recorded for barium sulphate in all the three orientations put together. Of these the Raman line at 620 wave numbers has not been observed before. The frequency shifts at 614 and 639 wave numbers respectively observed by Nisi but not by Rasetti have been confirmed by the author who has obtained them in two out of the three orientations. But Rasetti reports a line at 631 wave numbers which the author has not obtained in any of the three spectrograms. Similarly, the Raman