RAMAN SPECTRA OF CRYSTALLINE SULPHATES OF ZINC, MAGNESIUM AND SODIUM

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1. INTRODUCTION

A study of the Raman spectra of the sulphates in the form of single crystals is of interest in view of the information it will provide regarding their lattice spectra, the symmetry of the SO4 ion in these crystals, and the influence of the water of crystallisation on their spectra. Further, some of the hydrated sulphates are efflorescent and the difficulties met with in recording their complete spectra, using λ 4048 and λ 4358 of mercury, are considerable (Bouhet and Lafont, 1949). Hence the author carried out an investigation of the Raman spectra of the hydrated sulphates of zinc, magnesium, magnesium-ammonium and sodium and also of Thenardite (anhydrous sodium sulphate), using the λ 2537 radiation of mercury as exciter, and the results are given below.

2. EXPERIMENTAL DETAILS AND RESULTS

In all these cases, the Raman spectra excited by λ 2537 were recorded with the help of a Hilger medium quartz spectrograph having a dispersion of about 140 cm.⁻¹ in the above region. Using a slit width of 0.035 mm., the time of exposure necessary to get a well exposed spectrogram was of the order of 16 hours.

Zinc and Magnesium Sulphates.—These have been studied in the past by Krishnamurthy (1930), Nisi (1931) and Rao (1941), Krishnamurthy utilized the powder technique, while the other two used single crystals. Among them Rao recorded the maximum number of lines, namely, eight (455, 613, 981, 1046, 1101, 3226, 3285 and 3458 cm.⁻¹) in the case of magnesium sulphate and eleven (57, 94, 252, 375, 447, 608, 986, 1120, 1057, 3207 and 3395 cm.⁻¹) with zinc sulphate. Recently a detailed investigation has been made of the Raman spectrum of Epsomite (MgSO₄·7H₂O) by Bouhet and Lafont (1949). These authors have confined themselves to a thorough analysis of the polarisation and intensities of the Raman frequencies due

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to the sulphate ion for different orientations of the crystal. But they have failed to record any of the low frequency lines.

The specimens used in the present investigation were grown from aqueous solutions by the method of slow evaporation. The crystals grown thus were always strongly elongated in the direction of the c-axis. The exciting radiation was incident on the b (010) face of the crystal and the transversely scattered light was taken along the c-axis. The frequency shifts of the 24 Raman lines observed with magnesium sulphate are 56, 75, 97, 118, 150, 252, 303, 445, 461, 609, 620, 986, 1059, 1064, 1076, 1098, 1134, 1148, 3185, 3228, 3338, 3406, 3446, and 3485 cm$^{-1}$ and those of the 23 lines with zinc sulphate are 56, 70, 104, 128, 151, 212, 252, 373, 396, 445, 461, 609, 620, 990, 1057, 1062, 1094, 1121, 1141, 3154, 3392, 3436 and 3512 cm$^{-1}$. All the Raman lines in these sulphates both in the high and low frequency regions appear very diffuse. In the case of magnesium sulphate, the group of lines at about $\sim 1105$ cm$^{-1}$ is extremely complex. It is present as a wide band extending from 1040 to 1170 cm$^{-1}$. However, closer examination reveals that this group consists of three intense doublets, whereas Bouhet and Lafont have reported the existence of fourteen lines in this region. But among these, eight are very feeble in intensity. The frequency shifts of the intense ones recorded by them agree well with those of the three doublets observed by the author. The very faint lines 449 and 615 cm$^{-1}$ reported by them could not be identified in the spectrum recorded by the author.

The low frequency lines of zinc sulphate are in general more intense than those of magnesium sulphate. All the seven lattice lines of magnesium sulphate and the four lattice lines 70, 128, 151 and 212 cm$^{-1}$ of zinc sulphate have been recorded for the first time. The line at 258 cm$^{-1}$ is strong in both sulphates. In the case of zinc sulphate, this line is accompanied on the low frequency side by a band which shows a faint maximum at 212 cm$^{-1}$.

**Magnesium-Ammonium Sulphate.**—The Raman spectrum of magnesium-ammonium sulphate was studied by Nayar (1938) who recorded two Raman lines of frequency shifts 3284 and 3399 cm$^{-1}$ and three bands of frequency shifts 2848, 3070 and 3192 cm$^{-1}$. The first two are due to water molecules, while the last three are to be attributed to the vibrations of the NH$_4$ ion. The present study reveals as many as 23 Raman lines of which eighteen have been recorded for the first time. The frequency shifts of these are 54 (4), 89 (3), 130 (7), 147 (5), 198 (5), 220 (1), 265 (2), 455 (12), 622 (7), 979 (20), 1061, 1072, 1091, 1102, 1127, 1141, 1433 (8), 1469 (1), 2830 (3), 3060, 3281 (5), 3331 (5) and 3396 (5) cm$^{-1}$. The figures within brackets give rough estimate of the relative intensities of the lines. Since the intense group of lines at