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 $\text{NH}_4$ 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
about 1100 cm\(^{-1}\) consists of close doublets, and appears to be in reality a number of close lines, the relative intensities have been left out.

*Thenardite and Glauber's Salt.*—Thenardite, the naturally occurring form of anhydrous sodium sulphate, was studied in the form of crystal powder by Krishnamurthy (1930). He recorded a single Raman line with a frequency shift of 996 cm\(^{-1}\). The Raman spectrum of Glauber's salt, which is the hydrated form of the same salt with 10 molecules of water of crystallisation, was photographed by Nisi (1931) and it exhibited three lines with frequency shifts 991, 1125 and 3438 cm\(^{-1}\).

The Raman spectrum of thenardite recorded by the author revealed the existence of 13 Raman lines, the frequency shifts of which are 52, 76, 122, 164, 451, 467, 609, 624, 665, 995, 1087, 1117 and 1133 cm\(^{-1}\). In the case of Glauber's salt the light was incident along the X-axis of the crystal and the scattered light was taken in the perpendicular direction. These crystals, themselves strongly efflorescent were almost reduced to powder after fifteen minutes of exposure to the strong ultraviolet source. Moreover, as the salt decomposed at 32·5° C., the heat due to proximity of the arc was found to be sufficient to melt the crystal. To overcome this difficulty the following method was used. A small brass box was provided with two quartz windows on adjacent sides, one for the incident light and the other for the transversely scattered light. The lid of this box was closed airtight by means of vacuum grease. To one of the sides of the box was attached a short brass rod and this was kept at the centre of a copper vessel containing a mixture of ice and salt. The crystal was kept in the desired orientation inside the box and the above-mentioned arrangement served to maintain the crystal at a temperature far below its melting point and thus prevent the decomposition of the crystal. The frequency shifts of the lines recorded are 53, 134, 158, 231, 292, 441, 463, 571, 590, 609, 627, 992, 1088, 1117, 1136, 3271, 3332, 3378, 3438 and 3516 cm\(^{-1}\).

3. Discussion

*Zinc and Magnesium Sulphates.*—These are isomorphous and form double salts in any proportion. At ordinary temperatures they crystallise in the orthorhombic system with seven molecules of water of crystallisation and belong to the point group \(D_3\) and consequently possess three binary axes of symmetry. The unit cell contains 4 molecules. It is easily seen that in both cases the number of lattice lines observed is very small compared to that which can be theoretically expected. However, it is reasonable to suppose that of the theoretically possible ones, the rotatory type of lattice oscillations has negligible intensity as the polarisability of the free \(SO_4\) ion
is known to be spherically symmetric and is not distorted very much in the crystal. In addition, some of the lattice oscillations may have nearly the same frequency, but to establish this it is necessary to study the intensity and polarisation of the lattice lines for different orientations.

**Frequencies of the $SO_4$ Ion.**—The proper symmetry of the $SO_4$ ion in zinc and magnesium sulphates is no longer $T_e$ but only $C_1$. However, X-ray studies show that one of its planes of symmetry coincides with the XZ plane of the crystal with its two-fold axis making an angle of about $35^\circ$ with the $Z$-axis. Due to the lower symmetry, the degenerate oscillations of the free ion split in the crystal, so that all the nine distinct modes of the free $SO_4$ ion can appear in Raman effect. Further as there are 4 such groups in the unit cell and each oscillation by coupling can give rise to 4 internal oscillations of the crystal, one totally symmetric and the other three antisymmetric with respect to the binary axes of symmetry, there are 36 Raman active frequencies due to the sulphate ion. Of these 9 belong to the totally symmetric class and the remaining 27 to the antisymmetric class. Following the method adopted by Couture (1947) in the case of barytes and celestite, Bouhet and Lafont (1949) have been able to study the tensor appertaining to the variations of polarisability for the different oscillations and for different orientations of the crystal and assign the observed frequencies to the various possible internal oscillations of the $SO_4$ ion. The frequencies observed by the author in the case of Epsomite and included in Table I are in agreement with those of Bouhet and Lafont. However, the small splitting due to the presence of 4 sulphate groups could not be identified by the author as separate lines as the spectrograph used had a dispersion of about 140 cm.$^{-1}$ only. A comparison of the results obtained in the case of magnesium and zinc

<table>
<thead>
<tr>
<th>Type</th>
<th>MgSO$_4$·7H$_2$O</th>
<th>Type</th>
<th>ZnSO$_4$·7H$_2$O</th>
</tr>
</thead>
<tbody>
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<td>$B_1$, $B_2$</td>
<td>445</td>
</tr>
<tr>
<td>$B_3$</td>
<td>461</td>
<td>$B_3$</td>
<td>461</td>
</tr>
<tr>
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<td>$A_1$</td>
<td>609</td>
</tr>
<tr>
<td>$B_1$, $B_2$</td>
<td>620</td>
<td>$B_1$, $B_2$</td>
<td>620</td>
</tr>
<tr>
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<td>$A_1$</td>
<td>980</td>
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<td>$A_1$</td>
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</tr>
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<td>$B_3$</td>
<td>1062</td>
</tr>
<tr>
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<td>$A_1$, $B_1$, $B_2$</td>
<td>1094</td>
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<tr>
<td>$A_1$, $B_3$, $B_1$</td>
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<td>$A_1$, $B_2$</td>
<td>1121</td>
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<td>$A_1$</td>
<td>1134</td>
<td>$B_1$, $B_3$</td>
<td>1141</td>
</tr>
<tr>
<td>$B_1$, $B_3$</td>
<td>1148</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE I
Raman Spectra of Crystalline Sulphates

sulphates, in the light of the above-mentioned work of Bouhet and Lafont enables one to assign the observed frequencies as in Table I above.

Water Bands.—Hibben reported the existence of five water bands with frequency shifts at 3184, 3227, 3404, 3445, and 3481 cm\(^{-1}\) in the case of magnesium sulphate and three at 3151, 3436 and 3503 cm\(^{-1}\) in the case of zinc sulphate. The spectra recorded by the author exhibits in addition to these, one band at 3328 cm\(^{-1}\) in magnesium sulphate and one at 3342 cm\(^{-1}\) in the case of zinc sulphate. In Table II are given the frequency shifts corresponding to the maxima of water bands in crystalline magnesium and zinc sulphates recorded by the author and those in manganous and ferrous sulphates heptahydrates investigated by Rao (1951).

**Table II**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Maxima of water bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO(_4).7H(_2)O</td>
<td>3185 3228 3328 3406 3485</td>
</tr>
<tr>
<td>ZnSO(_4).7H(_2)O</td>
<td>3154 3342 3436 3512</td>
</tr>
<tr>
<td>FeSO(_4).7H(_2)O</td>
<td>3225 3337 3432 3543</td>
</tr>
<tr>
<td>MnSO(_4).7H(_2)O</td>
<td>3399 3467 3543</td>
</tr>
</tbody>
</table>

The bands which exist in common to all the sulphates are the ones in the region of 3350 and 3450 cm\(^{-1}\). Apart from this no direct relation seems to exist in the characteristics of the water bands of these sulphates though all of them have analogous crystal structure and contain the same number of molecules of water of crystallisation.

Magnesium-Ammonium Sulphate.—This double sulphate of magnesium and ammonium crystallises in the monoclinic system with six molecules of water of crystallisation. The space group is C\(_\text{2h}\) and the unit cell contains 2 molecules of MgSO\(_4\)(NH\(_4\))\(_2\)SO\(_4\).6H\(_2\)O. The character table derived by taking magnesium ion, ammonium ion and sulphate ions as separate groups and neglecting the water of crystallisation shows that there should be 12 rotatory and 12 translatory types of lattice oscillations active in Raman effect. But in the spectrogram only seven are observed and the difference might be due to the same reasons as those given in the case of zinc and magnesium sulphates. However, there is a great similarity between the lattice spectrum of MgSO\(_4\).7H\(_2\)O and that of the double sulphate.
**Internal Oscillations.**—Due to the low symmetry of the SO$_4$ ion in this crystal there is a removal of the degeneracy as in the cases studied above and the four distinct frequencies of the free tetrahedral SO$_4$ ion split up into 9 distinct modes and a further splitting also is caused by the coupling of the four SO$_4$ ions which the unit cell contains. The recorded spectrum exhibits 10 Raman lines which can be attributed to these. However, for a detailed analysis, polarisation data are necessary.

**Frequencies due to the NH$_4$-Ion.**—In contrast to the complete removal of degeneracy observed in the case of the SO$_4$ ion we find that only four lines which can be attributed to the NH$_4$ ion are present in the crystal though all of them have frequency shifts higher than the known frequencies of the free NH$_4$ ion.

In fact no line corresponding to $v_2 (3162 \text{ cm.}^{-1})$ of the free ion could be identified in this case.

**Water Bands.**—The spectrum due to the water of crystallisation consists of only a very broad and intense band with three maxima at 3281, 3331 and 3396 cm.$^{-1}$, which coincide approximately with a few of the bands observed with Epsomite.

**Thenardite and Glauber’s Salt.**—The crystal of thenardite belongs to the orthorhombic bipyramidal class and the space group is $Vh$$_h$. The unit cell contains eight molecules of Na$_2$SO$_4$. Glauber’s salt crystallises in the monoclinic class with well-developed $c$ (001) and $a$ (100) faces. Details regarding its structure are not known.

In Table III are given the internal frequencies of thenardite and Glauber’s salt along with the corresponding frequencies of the free sulphate ion.

![Table III](image)
It is noticed that all the degenerate lines split up into the corresponding components. All the lines are broad and diffuse in the case of Glauber's salt, while they are quite sharp in thenardite. This diffuse nature of the Raman lines is prominent in all the sulphates, so far studied, which possess water of crystallisation. Embirikos (1930) has also observed that the lines become more diffuse with increasing number of molecules of water of crystallisation.

Like the other sulphates, thenardite and Glauber's salt give only a comparatively small number of lattice lines despite the fact that theoretically many more can be expected.

The five high frequency lines which appear in the spectrum of Glauber's salt, namely 3271, 3332, 3378, 3438 and 3516 are to be attributed to the water molecules.

In conclusion the author wishes to express her sincere thanks to Professor R. S. Krishnan for suggesting the problem and for his help and guidance.

**Summary**

The Raman spectra of single crystals of the sulphates of zinc, magnesium, magnesium-ammonium and sodium (both thenardite and Glauber's salt) have been investigated using the $\lambda 2537$ resonance radiation of mercury as exciter. The important results obtained may be summarised as follows:

The Raman spectra of thenardite, the anhydrous sodium sulphate and of magnesium-ammonium sulphate have been recorded for the first time. In the case of the sulphates of zinc, magnesium and sodium (Glauber's salt) the recorded spectra indicate the existence of 23, 24 and 20 frequency shifts of which 16, 11 and 17 respectively are newly reported. The low frequency spectrum in each case has the following shifts:

(a) Zinc: 56, 70, 104, 128, 151, 212, 252 and 373 cm$^{-1}$;  
(b) Magnesium: 56, 75, 97, 118, 150, 252 and 303 cm$^{-1}$;  
(c) Magnesium-ammonium: 54, 89, 130, 147, 198, 220 and 265 cm$^{-1}$;  
(d) Thenardite: 52, 76, 122 and 164 cm$^{-1}$; and  
(e) Glauber's salt: 53, 134, 158, 231 and 292 cm$^{-1}$. The Raman lines of the hydrated sulphate are found to be more diffuse than the corresponding lines of the anhydrous sulphate. The results obtained have been discussed in the light of the known structures of these crystals.
REFERENCES

Krishnamurthy  .. *Nature*, 1930, 126, 169.

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(1) Na₂SO₄  (2) Na₂SO₄·10H₂O  (3) ZnSO₄·7H₂O  (4) MgSO₄·7H₂O