

THE RAMAN SPECTRA OF CRYSTALLINE SULPHATES OF Ni AND Mn

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(Memoir No. 112 from the Raman Research Institute, Bangalore-6)

Received November 24, 1958

(Communicated by Sir C. V. Raman)

1. INTRODUCTION

BELOW 31.5° C. nickel sulphate crystallizes from solution as $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in the orthorhombic system. Above this temperature it occurs as crystals of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ of the tetragonal system and these crystals undergo a transformation to the monoclinic form at 53.3° C. A study of the Raman spectra of these different modifications is obviously of much interest. The Raman spectra of the tetragonal and the orthorhombic varieties of nickel sulphate were reported by the author in an earlier paper; but the results therein were not complete owing to the experimental difficulties met with in recording the spectra of these crystals which are efflorescent. With improved experimental techniques and by the use of larger crystals it has now been possible to obtain fuller information regarding the Raman spectra of nickel sulphate in the tetragonal, orthorhombic and the monoclinic forms. In addition to these results, the present paper reports the details of a study undertaken for the first time on the Raman spectrum of manganese sulphate tetrahydrate.

2. EXPERIMENTAL DETAILS

The crystals of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ were grown from aqueous solution by the method of slow evaporation at room temperature. The crystals of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ were in the form of elongated tablets upto 5 cm. in length. The crystals of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ occurred as large thick rhombic tablets. Crystals of tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ upto a size of 2 cm. square were found to crystallize from solution during the course of particularly warm days of summer. Crystals of the monoclinic $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, however, could not be grown in sufficiently large sizes, although several attempts were made to grow them inside a thermostat at about 60° C. The small crystals grown at this temperature were confirmed to belong to the monoclinic variety from the biaxial figure of small axial angle expected to be exhibited by these crystals under the polarising microscope (Winchell, pp. 225). The tetragonal and orthorhombic crystals of nickel sulphate

were easily identified as such from their external form and depth of colour, and the respective uniaxial and biaxial interference figures exhibited by them served to confirm their identification. The crystals of manganese sulphate were found to be biaxial. They were identified as $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ belonging to the monoclinic system, in view of the close agreement of the observed specific gravity of 2.25 for these crystals with the value of 2.26 given by Winchell.

The Raman spectra were recorded with a medium Hilger quartz spectrograph and using the $\lambda 2536.5$ resonance radiation of mercury for the excitation of the Raman effect. A large Littrow quartz spectrograph was also used to record the spectra in the case of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. Full details of the experimental set-up have appeared in an earlier paper by the author. All these crystals were efflorescent and were reduced to an opaque white mass after a short exposure to the heat of the quartz arc. This necessitated that the crystals be placed at a safe distance from the arc. In spite of this precaution the crystals deteriorated rapidly and fresh crystals had to be used frequently. In the case of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ this precaution was particularly necessary since after losing a single water molecule they were transformed into the more stable tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

To record the spectrum of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ above the transformation point, a large tetragonal crystal was chosen and fixed in a brass rod, the lower end of which was immersed in a trough of boiling water and from which steam was rising continuously. Under these conditions the temperature in the neighbourhood of the crystal was about 60°C . It took about half an hour for the crystal to attain the steady temperature of 60°C . and in the process the clear tetragonal crystal was transformed into a translucent polycrystalline mass of the monoclinic variety. Very intense spectra in this case could not be obtained since the parasitic illumination from the polycrystal set a limit to the useful exposure that could be given. While in the other cases exposures of the order of 36 hours were given to obtain intense records of the spectra, exposures of only eight hours could be given in this case.

3. RESULTS AND DISCUSSION

Figs. 2, 3, 4 and 5 in the accompanying Plate reproduce the spectra obtained with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (tetragonal), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (monoclinic), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ respectively. Figs. 1 and 6 of the same Plate show the spectrum of the mercury arc for comparison. Figs. 1, 2, 3 and 4 appearing in the text are the microphotometer records of the spectra with the frequency shifts indicated therein. Table I exhibits the frequency shifts observed in all the four cases.

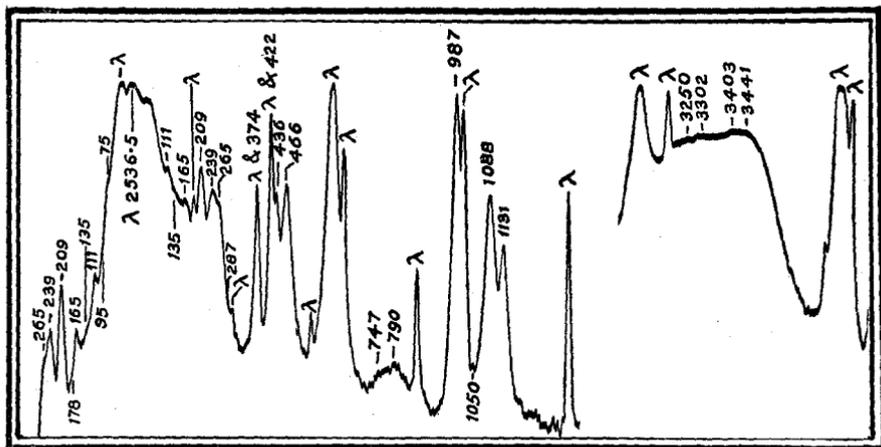


FIG. 1. Microphotometer Record of the Raman Spectrum of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Tetragonal).

The group of lines at about 620 cm.^{-1} (ν_3) in the case of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (tetragonal) and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ were observed as anti-Stokes shifts. On the Stokes side only the shifts 620, 620, 622 and 624 could be observed in the four cases. The other components could not be detected owing to the presence in this region of the strong mercury line $\lambda 2576.3$ and its satellite $\lambda 2578.4$.

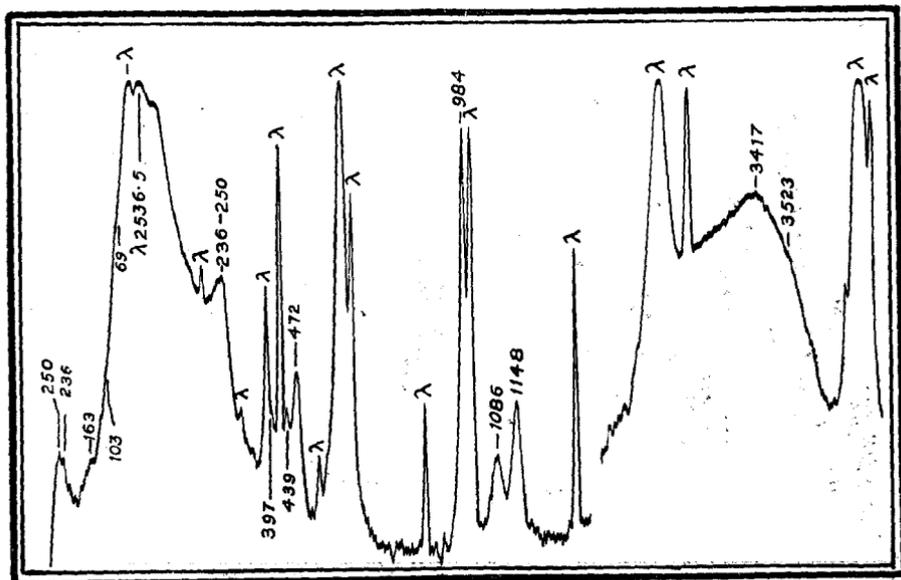


FIG. 2. Microphotometer Record of the Raman Spectrum of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Monoclinic).

Similarly the frequency shifts at about 185, 380 and 420 cm^{-1} shown in Table I were discovered on the anti-Stokes side since on the Stokes side there appear at about these points the mercury lines $\lambda 2548.6$, $\lambda 2561.2$ and $\lambda 2563.9$. The frequency shift at 971 cm^{-1} close to the intense line 987 cm^{-1} as well as those at 596 and 620 cm^{-1} in the case of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were manifest in the spectra recorded by the Littrow spectrograph.

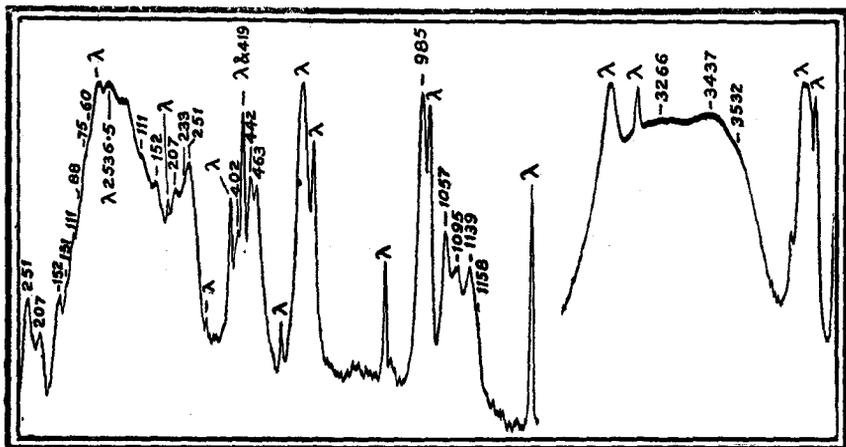


FIG. 3. Microphotometer Record of the Raman Spectrum of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.

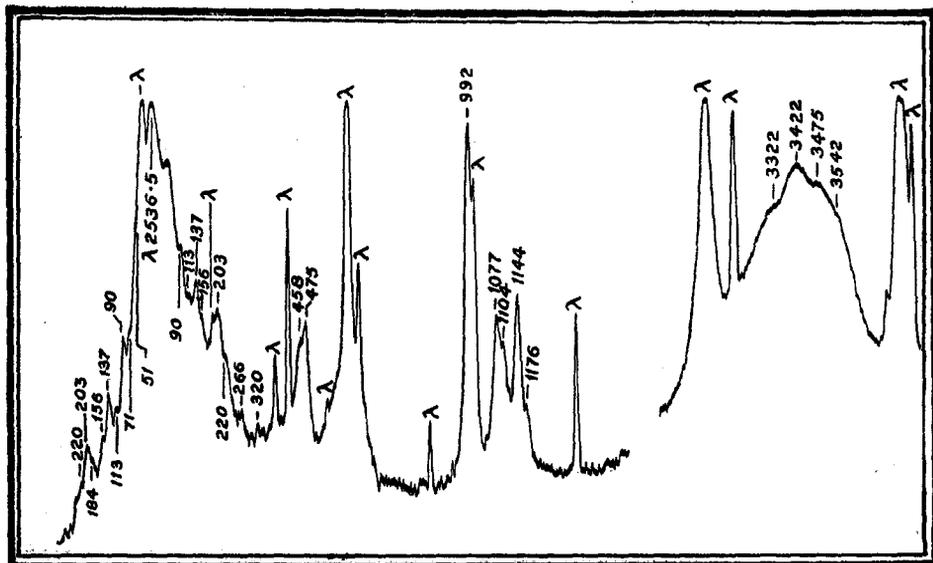


FIG. 4. Microphotometer Record of the Raman Spectrum of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.

TABLE I
Frequency Shifts in cm.^{-1}

	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ Tetragonal	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ Monoclinic	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$
Lattice Oscillations	75 s. 95 w. 111 s. 135 v.w. 165 s. 178 v.w. 209 v.s. 239 s. 265 s. 287 v.w.	69 s. 103 w. 163 m. 236 m. 250 s.	60 m. 75 s. 88 m. 111 s. 131 w. 152 s. 207 s. 233 w. 251 v.s.	51 s. 71 m. 90 s. 113 w. 137 s. 156 w. 184 w. 203 s. 220 m. 266 w.d. 320 w.d.
ν_2	374 m. 422 m. 436 s. 466 s.	397 m. 439 m. 472 s.	402 m. 419 w. 442 s. 463 s.	 458 m. 475 s.
ν_3	596 m. 620 s. 639 s.	620 m.	612 s. 622 w. 642 m.	624 m.
ν_1	971 w. 987 v.s.	984 v.s.	985 v.s.	992 v.s.
ν_4	1050 v.w. 1088 s. 1131 m.	1086 m. 1148 s.	1057 s. 1095 m. 1139 m. 1158 w.	1077 s. 1104 m. 1144 s. 1176 w.
Water Bands	3250 s. 3302 s. 3403 v.s. 3441 v.s.	3417 v.s. 3523 m.	3266 m. 3437 v.s. 3532 w.	3322 m. 3422 v.s. 3475 s. 3542 m.

s. = Strong; w. = Weak; v.s. = Very Strong; v.w. = Very Weak; m. = Medium;
d. = Diffuse.

The observed frequency shifts may readily be seen to fall distinctively into six classes. The frequency shifts upto 320 cm.^{-1} in Table I, all arise due to the rotational and translational oscillations against each other of the ions and water molecules constituting the unit cell of the crystal structure,

Beyond this region we have specific groups of frequency shifts centred at 450, 620, 980 and 1100 cm^{-1} and which frequency shifts correspond respectively to the (1) doubly degenerate, (2) triply degenerate, (3) totally symmetric and (4) triply degenerate normal modes of vibration of the free SO_4 ion. Lastly we have the broad and diffuse bands characteristic of the water, in the region of frequencies 3200 to 3600 cm^{-1}

In addition to these general features the spectra of the four crystals exhibit several special characteristics of interest. It may be noticed from Table I that in the lattice frequency region striking correspondences exist between the numerical values of the observed frequency shifts. However, an examination of Plate XXX reveals at once that such agreement is not always found to be present with regard to the intensities of the corresponding lines. It may be noticed in particular that the intense frequency shift at 209 cm^{-1} observed in the tetragonal form of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is totally absent in the case of the monoclinic form. In addition, the lattice spectrum in the latter case is smeared out into a diffuse band of illumination with a few definite frequency shifts. Another feature of interest is with regard to the varying multiplicity and relative intensity of the frequency shifts of the SO_4 ions in the different crystals. We shall here seek to explain these features in the light of our knowledge of the crystal structures of these substances.

(1) *NiSO₄·6H₂O (tetragonal)*. The crystal structure of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ at ordinary temperatures has been determined by Beevers and Lipson (1932) and assigned to the space-group P4_12_12 (D_4^4) of the enantiomorphous hemihedral class of the tetragonal system, with four molecules in the unit cell. The nickel and sulphur atoms occupy the special positions of the symmetry of a two-fold axis of rotation. All the other atoms occupy general positions and the six water molecules are octahedrally co-ordinated around the nickel atom. The normal modes of vibration of the system belonging to the symmetry D_4 fall into five representations A_1 , A_2 , B_1 , B_2 and E , A_2 being Raman inactive, and A_1 , B_1 and B_2 being infra-red inactive. A study of the infra-red absorption of these crystals would be of value in assigning the frequencies to the different classes.

Since the local symmetry of the SO_4 ion is only C_2 in the crystalline state, the degeneracies are removed and nine frequencies in all (to a first approximation) should manifest themselves in the spectrum. But, owing to the fact that there are four molecules in the unit cell, the number of components is further increased. Group-theoretical analysis shows that in this case the total number of components is twenty-seven, of which twenty-two should be observed in the Raman effect. In all, the spectrum exhibits twelve compo-

nents, some of which are rather broad. The fact of some of the components being too weak, or of their overlapping with each other, might account for the reduced number of observed components. Two broad and weak bands at about 747 and 790 cm^{-1} are also observed in the spectrum. Their origin is however not quite clear.

(2) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (*orthorhombic*). $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ had been found to belong to the space-group $\text{P2}_12_12_1$ (D_2^4) of the enantiomorphous hemihedral class of the orthorhombic system (Beevers and Schwartz, 1935). All atoms are situated in general positions and the structure is similar to that of the tetragonal hexahydrate with four molecules in the unit cell and with six of the water molecules co-ordinated octahedrally around the nickel atom and the seventh water molecule occupying an interstitial position filling what would otherwise be a hole in the structure. Considerations similar to those put forward in the previous case indicate that due to the internal vibrations of the four SO_4 ions in the unit cell thirty-six components should appear in the Raman effect and twenty-seven in the infra-red. However, apparently for the reasons advanced already, only twelve components—some of which are rather broad—are observed.

The general similarity of the lattice spectrum of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (*orthorhombic*) with that of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (*tetragonal*) has its origin in the similarity of the crystal architecture in these two cases. The intensities of the lines, however, do not correspond, as is naturally to be expected from the fact of the crystals belonging to two different symmetry classes.

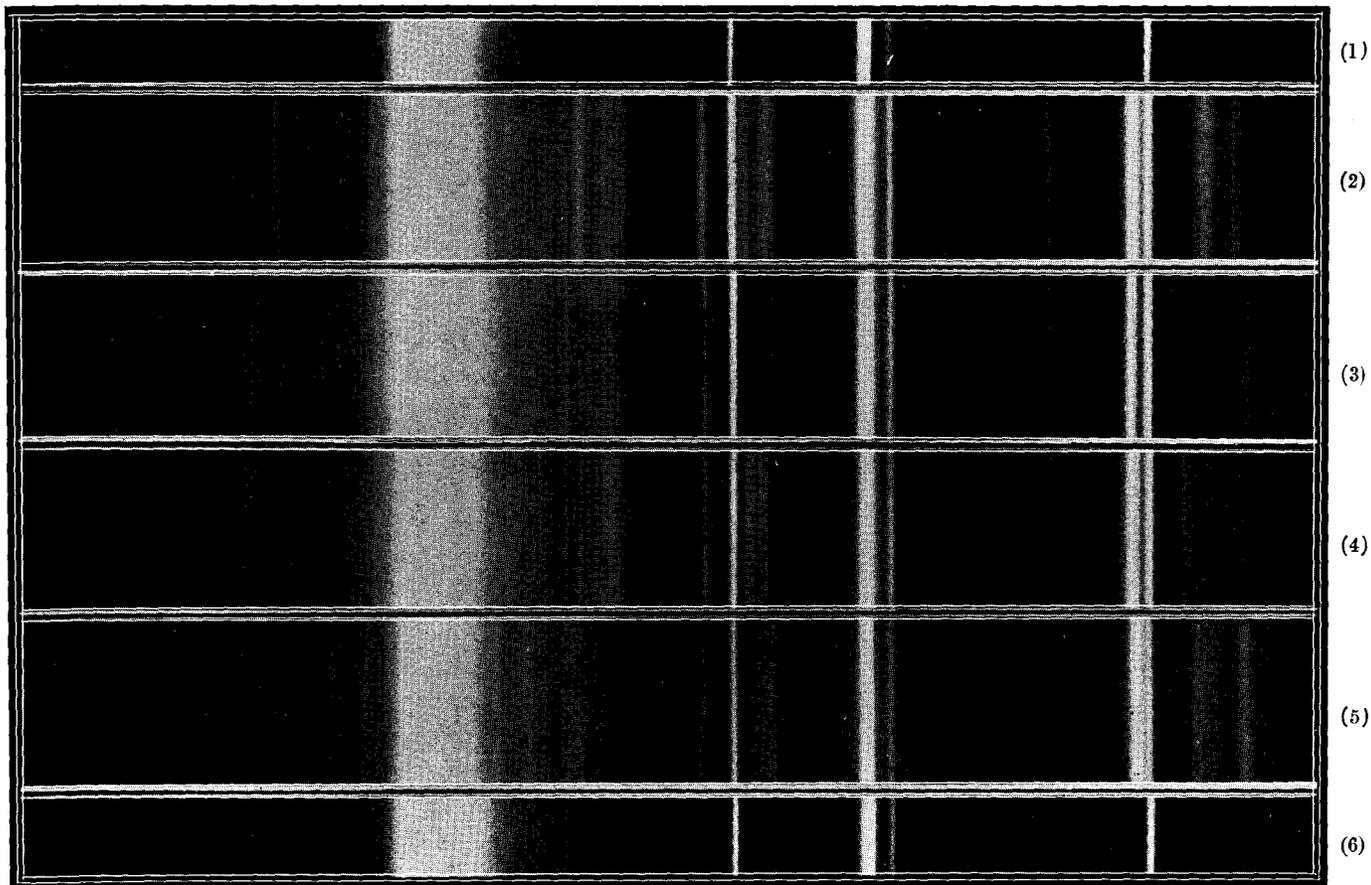
(3) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (*monoclinic*). Apart from the fact that the crystals of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ above 53.3°C . belong to the monoclinic system and exhibit a small optic axial angle of $19^\circ 25'$, no data regarding its crystal structure are to be found in the literature. In view of the small optic axial angle observed, it is probable that the monoclinic form of the crystal above 53.3°C . is derived from a distortion of the tetragonal structure observed at ordinary temperatures. In this case seven components corresponding to the internal frequencies of the SO_4 ion are observed. The fact of the doubly degenerate mode of the free ion manifesting itself as three distinct components in the spectrum of the crystal indicates that there are at least two, or more than two molecules in the unit cell of the crystal.

Crystals of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ exhibit optical characters similar to those of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (*monoclinic*) (*vide* Winchell, pp. 225 and 231). In addition, the values of the angle β are in good agreement, being respectively $81^\circ 26'$ and $81^\circ 43'$. The structure of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ has been found to belong to the space-group $\text{C2}/c$ (C_{2h}^6) of the monoclinic system and with eight molecules

in the unit cell (Wyckoff, 1951). The modes of vibration of a system belonging to the group C_{2h} fall into four groups, of which only two groups of symmetric vibrations are Raman active, the other two groups of anti-symmetric vibrations being Raman inactive. If it could be assumed as stated by Sidgwick (1950) that the structure of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (monoclinic) is isomorphous with the above $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, we can account for the fact of some of the frequencies like the 209 cm.^{-1} observed in the tetragonal form being totally absent in the monoclinic form. A correspondence could then exist between the vibrations of these two systems and one set of modes present in the tetragonal form would vanish in the monoclinic form. In this respect the numerical agreements between some of the frequencies of the tetragonal form and those of the monoclinic form are also noteworthy. The diffuse nature of the lattice spectrum may have its origin in that the spectrum was recorded at a temperature of 60° C. which is quite close to the transformation temperature of 53.3° C.

(4) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. No data regarding the crystal structure of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ are available and only its optical characters are known. From the optical data these crystals are known to belong to the monoclinic system. In the case of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ eight frequency shifts due to the internal vibrations of the SO_4 ions are observed. In particular, the triply degenerate mode, corresponding to the free ion, manifests itself in the crystalline state as four distinct components, thereby indicating that there is more than one molecule in the unit cell of the crystal structure. The lattice spectrum of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ exhibits close similarities with those observed for $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (tetragonal) and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. The atomic weights of nickel and manganese are not very different (being 58.69 and 54.93 respectively) and hence those normal modes which are essentially similar with regard to their rotational or translational characters in the case of these crystals would have nearly equal frequencies. Another noteworthy feature is the comparatively sharp water bands exhibited by $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ unlike those observed in the other cases. The fewer number of water molecules in this case may be the reason for this feature. However, it is not directly possible to correlate the differences observed (in the four cases) with regard to the water bands.

Lakshman Rao (1942) reports for the Raman spectrum of $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ seven lines at 330, 457, 603, 693, 994, 1085 and 1148 cm.^{-1} and two bands due to the water of crystallisation at 3399 and 3467 cm.^{-1} . It may be noticed that the frequencies reported by him and those emerging from this study are not in agreement. In particular, the present study does not reveal the existence of lines at 330 and 693 cm.^{-1} even though it is perfectly possible for



Raman Spectra of Crystalline Sulphates. Fig. 2. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (*tetragonal*). Fig. 3. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (*monoclinic*). Fig. 4. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. Fig. 5. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. Figs. 1 and 6. Spectrum of the mercury arc.

them to be recorded and observed if present. Lakshman Rao also states that the crystallisations were carried out at about 27° C. It appears that the crystals used by Lakshman Rao were not $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ since $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ is stable only upto 6° C. They could not have been $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ for reasons of disagreement of his results with those of the present study. MnSO_4 is known to crystallize with five molecules of water of crystallisation between 6° and 20° C. It is quite probable that his results refer to $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. Apart from the few infra-red frequencies at 635, 1111, 1116, 2940, 3030 and 3125 cm^{-1} reported by Schaefer and Schubert (1916) from studies on infra-red reflection by $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (tetragonal) no data are available regarding the infra-red spectra of these crystals for correlation with the Raman frequencies.

In conclusion, the author expresses his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for his kind interest in this investigation.

SUMMARY

The paper reports the results of investigations on the Raman spectra of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (tetragonal and monoclinic forms), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (orthorhombic) and $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (monoclinic). Using $\lambda 2536 \cdot 5$ resonance radiation of mercury for excitation of the Raman effect, it has been possible to observe a large number of frequency shifts. The spectra exhibit striking differences between themselves and also a few characters of general similarity. These are largely explicable in terms of the crystal symmetry and structure of these substances. In all the cases studied, the internal frequencies of the sulphate ion exhibit multiplicities owing to the lowering of the symmetry of the SO_4 ion in the crystalline state and due to the number of ions present in the unit cell.

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