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RAMAN SPECTRA OF NICKEL SULPHATE CRYSTALS

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1. INTRODUCTION

NICKEL sulphate crystallizes from solution at room temperature (30° C.) as $NiSO_4.7H_2O$ in the orthorhombic system. At about 35° C it crystallizes as $NiSO_4 \cdot 6H_2O$ in the tetragonal system, while at about 60° C. it crystallizes as $NiSO_4 \cdot 6H_2O$ but in the monoclinic system. The complete Raman spectrum of crystalline nickel sulphate has not so far been reported since the λ 4358 and λ 4046 radiations of the mercury arc ordinarily employed are absorbed. Nisi (1930) using the group of lines at λ 3126 in the mercury arc spectrum has reported in the case of $NiSO_4 \cdot 7H_2O$ the principal sulphate frequency of shift 985 cm.$^{-1}$ and two water bands at 3209 and 3432 cm.$^{-1}$

The absorption in the near ultraviolet for nickel sulphate lies at λ 3850 and the crystals are transparent to radiations of shorter wavelengths over a wide range in the ultraviolet. The present paper reports the results of an investigation with the orthorhombic and tetragonal crystals using the resonance radiation λ 2536·5 of the mercury arc for exciting the Raman effect.

2. EXPERIMENTAL DETAILS

The crystals of $NiSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ were grown by the method of slow evaporation, the latter at a temperature of 35° C. in a thermostat. The crystals of $NiSO_4 \cdot 6H_2O$ were of a deeper green in colour than those of $NiSO_4 \cdot 7H_2O$. The biaxial nature of the interference figures in the case of $NiSO_4 \cdot 7H_2O$ and the uniaxial nature of the figures of $NiSO_4 \cdot 6H_2O$ observed under the polarising microscope confirmed their respective identification from depth of colour and external form. The crystals of $NiSO_4 \cdot 7H_2O$ were in the form of rectangular tablets of size 20 mm. × 10 mm. × 2 mm. The crystals of $NiSO_4 \cdot 6H_2O$ which were pyramidal in form were rather small. Since both the crystals were efflorescent, a thin film of glycerine was put over them to reduce the rate of efflorescence. However, the crystals of $NiSO_4 \cdot 7H_2O$ deteriorated rapidly and fresh crystals had to be used frequently.

The Raman spectra were recorded with a Hilger medium quartz spectrograph having a dispersion of 140 cm.$^{-1}$ per mm. in the λ2536·5 region. A water-cooled magnet controlled quartz mercury arc served as an intense source of λ 2536·5. The crystals were placed near the arc and the scattered radiations were focussed on the slit of the spectrograph with a quartz condenser. The scattered resonance radiation was filtered out by the mercury vapour inside the spectrograph. With a slit width of 0·04–0·05 mm., exposures of the order of ten hours were given to obtain reasonably intense spectrograms.

3. RESULTS

Figs. (1) and (2) in the accompanying Plate reproduce the spectra obtained with $NiSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ respectively. The lowermost part of the spectrum in Fig. 2 which is very intense due to parasitic light helps to identify the lines of the mercury arc.

An examination of the spectra of the two crystals reveals the following features: (1) The low frequency spectra of these crystals are faint and

TABLE I

Frequency Shifts in cm.⁻¹

	$NiSO_4 \cdot 7H_2O$	$NiSO_4 \cdot 6H_2O$
Lattice Oscillations	~ 75 v.w. ~ 110 v.w. ~ 156 w. 210 m. 255 b.m.	210 m. 236–69 b.m.
ν_2	400 w. 444 s. 465 s.	440 s. 469 s.
ν_3	620 ?	620 ?
ν_1	986 v.s.	988 v.s.
ν_4	1060 b.s. 1098 b.m. 1138 b.s. ~1165 v.w.	1092 b.s. 1133 b.s.
Water Bands	~3282 v.s. ~3438 v.s.	~3257 v.s. ~3439 v.s.

s., Strong; w., weak; v.s., very strong; v.w., very weak; m., medium; b., broad.

~ value of the frequency shift estimated from the relative position of the line with respect to the neighbouring iron arc lines.

diffuse. (2) The frequency shifts due to the oscillations of the sulphate ions in the two crystals are different in the two cases. It may be noticed that the splitting of the doubly degenerate oscillation at 450 cm.$^{-1}$ is larger in the case of $NiSO_4 \cdot 6H_2O$ than in the case of $NiSO_4 \cdot 7H_2O$. Measurements indicate that the non-degenerate oscillation has a frequency shift of 986 cm.$^{-1}$ in the case of $NiSO_4 \cdot 7H_2O$, while in the case of $NiSO_4 \cdot 6H_2O$ it has a shift of 988 cm.$^{-1}$ It will also be noticed that the triply degenerate oscillation at 1100 cm.$^{-1}$ has split into more components in the case of $NiSO_4 \cdot 7H_2O$ which is of lower symmetry than $NiSO_4 \cdot 6H_2O$. The water bands also show differences in their structure in the two cases.

Table I gives the frequency shifts observed in the two cases. The frequency shifts of some of the lines which were faint and diffuse could only be approximately estimated. The sulphate ion frequency of shift about 620 cm.$^{-1}$ could not be unambiguously observed owing to the proximity of the intense mercury line at λ 2576.

4. DISCUSSION

$NiSO_4 \cdot 7H_2O$ has been assigned to the space group $P\,2_12_12_1\,(D_2^4)$ of the enantiomorphous hemihedral class of the orthorhombic system, whereas $NiSO_4 \cdot 6H_2O$ has been assigned to the space group $P\,4_12_12\,(D_4^4)$ of the enantiomorphous hemihedral class of the tetragonal system. (Beevers and Schwartz, 1935; Beevers and Lipson, 1932). In the case of $NiSO_4 \cdot 6H_2O$ the nickel and sulphur atoms occupy the special positions with the symmetry of the two-fold axis of rotation. The six water molecules are said to be approximately octahedrally co-ordinated around the nickel ions. On the other hand, in $NiSO_4 \cdot 7H_2O$ the nickel and sulphur ions do not occupy any such symmetric special positions. Six of the seven water molecules are approximately octahedrally co-ordinated around the nickel ions in this case as well. In the case of $NiSO_4 \cdot 7H_2O$ as well as in $NiSO_4 \cdot 6H_2O$ there are four molecules per unit cell.

The degradation of the symmetry of the sulphate ion in the crystalline state and the consequent removal of the degeneracy of the oscillations results in the splitting of the degenerate oscillations, and hence all the nine frequencies of the SO_4 ion should appear. The coupling between the four molecules in the unit cell further increases the number of these internal oscillations. Thus, in the case of $NiSO_4 \cdot 7H_2O$ thirty-six components should appear whereas in the case of $NiSO_4 \cdot 6H_2O$ this number is only twenty-four owing to the higher symmetry of the crystal. Though the theoretically expected multiplicity of lines is not fully manifested in the spectra, the differences in the nature of the spectra due to the difference in the crystal symmetry and structure are evident. The breadth of some of the lines (*e.g.*, the group near 1100 cm.$^{-1}$) might be attributed to the overlapping of several of the components and their inadequate resolution.

The Raman spectrum of $NiSO_4 \cdot 7H_2O$ exhibits a close correspondence with the spectrum of $MgSO_4 \cdot 7H_2O$ (Shantakumari, 1953) the crystal structure of which is isomorphous with that of $NiSO_4 \cdot 7H_2O$. The following frequencies have been reported by her. 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.$^{-1}$

Schaefer and Schubert (1916) report from their studies on the infra-red reflection spectrum of $NiSO_4 \cdot 6H_2O$, frequencies at 635, 1111, 1116, 2940, 3030 and 3125 cm.$^{-1}$ No infrared absorption studies appear to have been made with crystalline nickel sulphate.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for the kind interest that he took during the course of this investigation.

5. SUMMARY

The Raman spectra of orthorhombic $NiSO_4 \cdot 7H_2O$ and the tetragonal $NiSO_4 \cdot 6H_2O$ have been investigated using the resonance radiation of mercury for excitation. Readily observable differences are exhibited by the spectra in the two cases which may be ascribed to the differences in crystal structure and symmetry.

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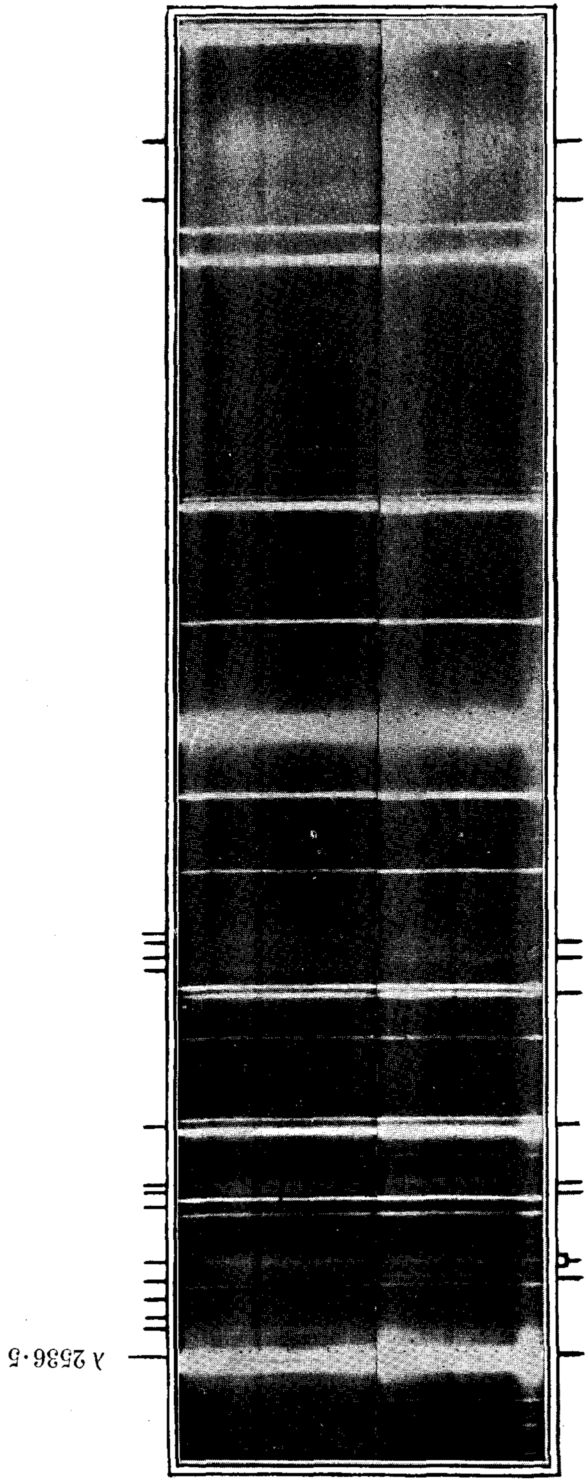
FIG. 1

FIG. 2



Raman Spectra of (1) $NiSO_4 \cdot 7H_2O$ and (2) $NiSO_4 \cdot 6H_2O$.