

Raman Effect in Single Crystal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

L. S. G. CANCELA* and G. M. GUALBERTO**

*Instituto de Física, UNICAMP, 13100 Campinas, Brasil****

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The Raman spectrum of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was obtained at room temperature and 77 K. A theoretical study of the number, type and activity of the optical phonons in this material, permitted a classification of the observed phonons. The data showed an anomalous temperature dependence for the peak at 42 cm^{-1} with symmetry B_2 and for the peaks at 75 and 115 cm^{-1} with symmetry A_1 .

O espectro Raman do $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ foi obtido à temperatura ambiente e a 77K. Um estudo teórico do número, tipo e atividades dos fonons ópticos neste material, nos permitiu classificar os fonons observados experimentalmente. Os resultados mostraram anomalias na dependência com a temperatura, para o pico em 42 cm^{-1} com simetria B_2 e para os picos 75 e 115 cm^{-1} com simetria A_1 .

INTRODUCTION

The Raman spectrum of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was studied by Stekhanov¹ in the neighborhood of the water vibrations between 2800 and 3700 cm^{-1} . He showed the influence of the crystal lattice on the vibrational spectrum of the hydrogen lines. Using a mercury lamp as the source, Krishnamurti² for the first time obtained a Raman spectrum at room temperature of sin-

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gle crystals of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Jäger and Schaak³ have reported the laser excited Raman and IR specular reflection spectra (below 1200 cm^{-1}) of the crystal and its deuterated analogue at different temperatures; however this study provides explanation which are inconsistent with the structural data of the crystal. Finally, Jain et al⁴ report a correct assignment of all phonons, as predicted by group theory. However those authors do not determine correctly all the phonon frequencies probably because the Raman measurements were performed at room temperature only. In the present work, we have made a theoretical study to determine the type, number and activity of the optical phonons. Furthermore, we have obtained the Raman spectrum of single crystals of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, at room temperature and at 77 K, using a laser as the excitation source.

The structure of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is well-known from x-ray studies⁵. The six water molecules form an octahedron around the nickel atom and the four oxygens form a tetrahedron around the sulfur. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is a hygroscopic crystal which crystallizes in the tetragonal group $D_4^h(P4_1 2_1)$ with four molecules per unit cell. The four SO_4^{--} ions are in sites with C_2 symmetry, as are the four Ni^{++} , whereas the 24 water molecules are in sites of C_1 symmetry. In ref.6 the tetragonal structure is shown projected onto one face of the cell.

Group theory predicts that the zone-center phonons belong to the following irreducible representations: $35 A_1 + 37 A_2 + 37 B_1 + 35 B_2 + 72 E$. The $35 A_1 + 37 B_1 + 35 B_2$ are Raman active optical phonons, the $36 A_2$ are infrared active and the $71 E$ are simultaneously Raman and infrared active. The degrees of freedom of the free SO_4^{--} ion are divided into the irreducible representations $A_1 + E + F_1 + 3F_2$. According to Herzberg⁷ they consist of the internal modes ν_1, ν_2, ν_3 and ν_4 , the rotation R_{xyz} and the translations T_{xyz} . The complex $\text{Ni}(\text{H}_2\text{O})_6^{++}$ form an octahedron in which the nickel occupies the center and is surrounded by the water molecules. The degrees of freedom of this complex can be divided into the irreducible representations $A_{1g} + E_g + F_{1g} + F_{2g} + 3F_{1u} + F_{2u}$. The symmetry mode A_{1g} consists of the internal mode ν_1^1 ; the doubly degenerate E corresponds to ν_2^1 , the triply degenerate F_{1g} to the rotations R_{xyz} ; the three F_{1u} modes corresponds to the translations T_{xyz} and the vibrations ν_3^1 and ν_4^1 and finally the mode F_{2u} , also triply degenerate, corresponds to the vibrations ν_6^1 . The diagram of Fig. 1 shows the development of the

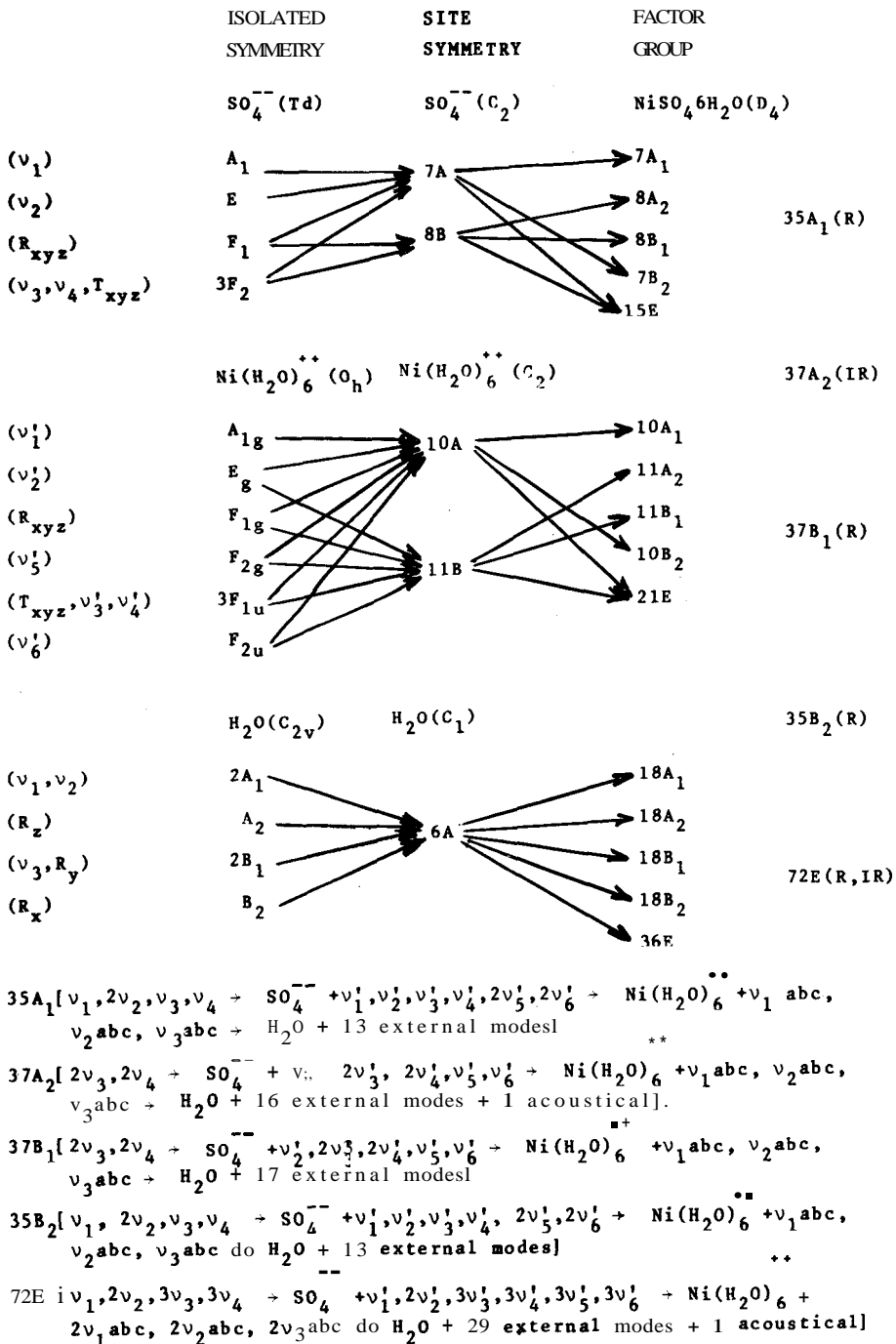


Fig.1 - Correlation table of $NiSO_4 \cdot 6H_2O$.

sites and the factor groups of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. The Raman tensors associated with each symmetry are given below⁸

$$A_1 = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}$$

$$B_2 = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$B_1 = \begin{bmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E(-y) = \begin{bmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{bmatrix}$$

$$E(x) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{bmatrix}$$

EXPERIMENTAL DETAILS

The single crystals of nickel sulfate used in these experiments were grown at a temperature of 38°C from a saturated solution. Using the Laue technique, we verified that the crystals grow along the 001 direction in the form of a truncated pyramid with the \underline{a} and \underline{b} axes parallel to the edges of the base. The \underline{A} and \underline{B} faces of the crystal were polished using cerium oxide and mineral oil while the \underline{C} face was obtained by cleaving the sample. Since the crystal is hygroscopic, the spectra are obtained soon after the crystal is polished. The source used was the 4880 \AA line of an argon laser since we confirmed that the absorption of this crystal⁹ is lowest around this line. The power used was limited to 50 mW since, with larger powers, the crystal soon became opaque. The scattered light was analyzed with a double Spex monochromator equipped with a F.W. 130 photomultiplier. For measurements at 77 K , an immersion dewar was used. In this work the scattering geometry is indicated by the usual Raman notation¹⁰ $k(ij)q$ where k and q indicate the directions of incident and scattered light, respectively, and i and j the polarization directions.

RESULTS AND DISCUSSIONS

In Fig. 2 we show the Raman spectrum of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ obtained using different geometries and temperatures to separate the various li-

nes. In this figure all of the spectra were obtained in the region 0 to 1200 cm^{-1} . In the neighborhood of the ν_2 mode of water ($\sim 1600 \text{ cm}^{-1}$) nothing was observed, while the ν_1 and ν_3 modes are seen in Fig. 3. The classification of the phonons of Fig. 2 is given in Table 1, for $T = 77\text{K}$

Table 1 - Optical phonons of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ at room temperature and 77K, all values are expressed in cm^{-1}

$A_1+x(zz)y$		$A_1+B_1 z(xxy)y$		$B_2 z(xxy)x$		$E(x) x(yz)y$	
300K	77K	300K	77K	300K	77K	300K	77K
75	80	34	35	42	46	54	55
115	111	44	49	140	146		67
164	169	67	73	208	213	74	79
	194	82	82	245	235	89	88
211	216	102	95		253		95
	241		103		275	107	106
270	279	114	107	294	300	125	130
295	303		110	370	382		139
375	379	130	137	417	424	142	145
425	430		146	439	436	154	163
	442		160	468	469	166	175
457	469		167	617	607	205	208
	473	217	210		629	239	247
603	594		220	806	766	266	283
	619	237	239		821	376	353
972	972		250		885		380
987	987	262	274	987	987	436	428
1088	1087	292	298	1100	1100		437
		322	328			466	466
		375	377				520
			392				559
		423	415			613	604
			430				655
		436	439			987	987
		463	455			1090	1090
			467			1129	1129
			474				
			521				
			568				
		613	595				
			616				
		743	758				
		865	867				
		972	972				
		987	987				
		1088	1088				
		1123	1123				

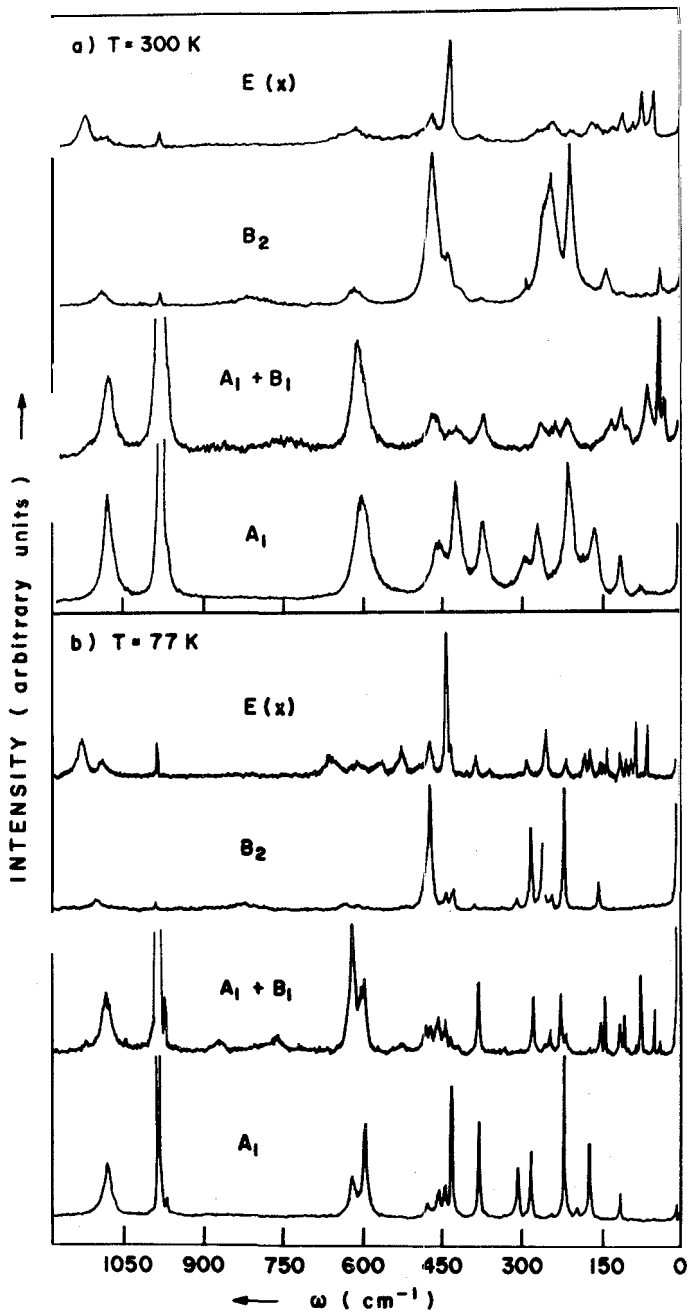


Fig.2 - Survey Raman Spectra of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. (a) Spectrum showing A_1 , $A_1 + B_1$, B_2 and $E(x)$ Phonons at room temperature. (b) Spectrum showing the same phonons at 77K.

and 300 K. In Fig. 2 we show the A_1 phonons which corresponds to the configuration $x(zz)y$, the B_2 corresponding to $z(xy)x$, the E for $z(yz)y$ and those for the geometry $z(xx)y$ which corresponds to a superposition of the phonons A_1 and B_2 . For the low temperature measurements, the resolution is better as we see in Fig. 2b. In these spectra, we see that, ex-

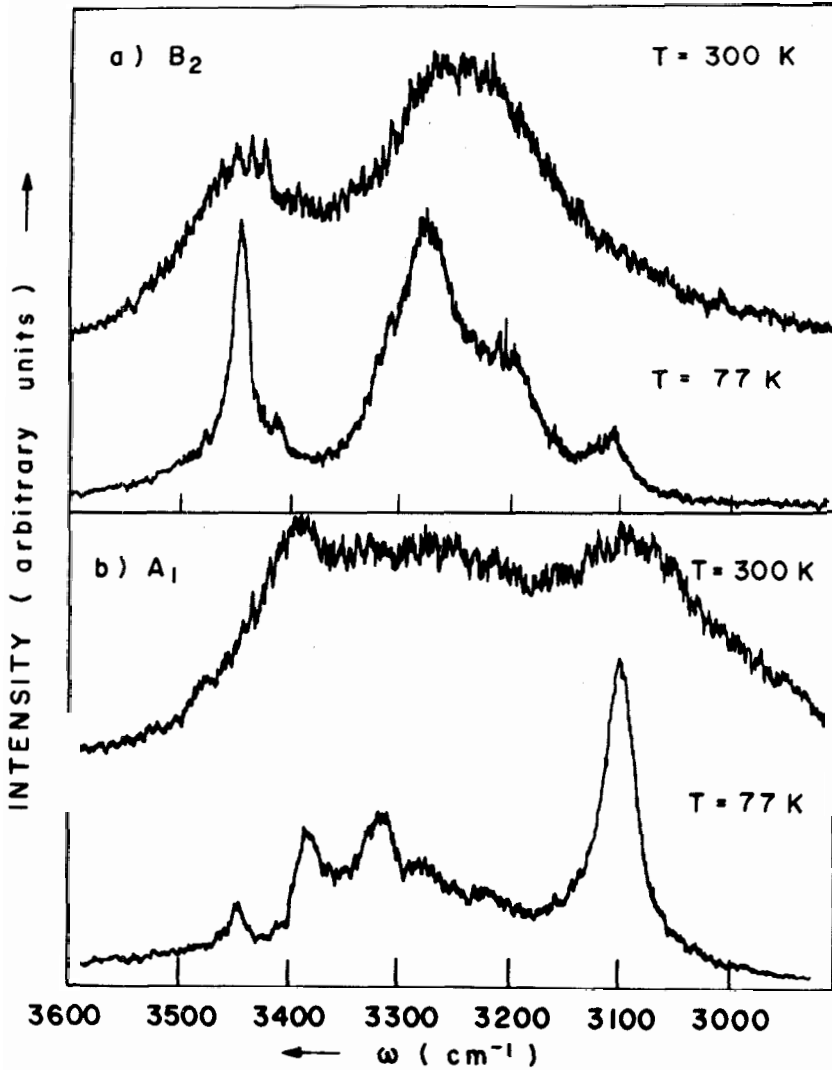


Fig.3 - Raman Spectrum of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in the H_2O internal mode region. (a) Spectrum Showing B_2 Phonons at 300 and 77K. (b) Spectrum showing A_1 phonons at 300 and 77K.

cluding the internal modes of water, we observe 18 of the 26 modes predicted for A_1 symmetry; 18 of the 26 predicted for B_2 symmetry, and 26 of the 62 predicted for $E(x)$ symmetry. For the geometry $z(xx)y$ we have a superposition of the A_1 and B_1 symmetries, where the frequencies 194cm^{-1} and 303cm^{-1} with A_1 symmetry have decreased in intensity to the point of being invisible on this scale. The phonons seen in this geometry and not in the $x(zz)y$ are classified as B_1 and they are 25 of the 28 predicted.

From the distribution of the water molecules in the unit cell⁶, we note that they are divided into three groups of eight molecules. Thus, we expect that in the region of the ν_1 and ν_2 modes there will be 6 peaks, corresponding to three modes for ν_1 and three for ν_2 . Fig. 3 shows the region between 3000 and 3600cm^{-1} where the ν_1 and ν_2 modes of water appear, for room temperature and 77K and for the A_1 and B_2 symmetries. Table 2 shows the vibrational frequencies of the OH group.

Table 2 - Frequencies (cm^{-1}) of Raman lines for $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in the H_2O internal modes region at 300 and 77K .

$A_1x(zz)y$		$B_2z(xy)z$	
300K	77K	300K	77K
3101	3101	3257	3113
	3220		3214
	3286		3289
	3325		3322
3400	3393	3458	3421
	3457		3458

CONCLUSION

As we see in Figs. 2 and 3 the temperature reduction was fundamental for a precise determination of the frequencies. The modes A_1 $x(zz)y$ and B_2 $z(xy)y$ show 13 frequencies at 300 K and 18 each at 77 K; the $E(x)$ $z(yz)y$ mode gave 18 frequencies at room temperature but 26 at 77 K; and finally, for the $A_1 + B_1$ modes, the number increased from 23 to 37 at 77 K. For the internal modes (Fig.3) the effect of the temperature is even more pronounced. At room temperature, the overlap of the lines results in two peaks with symmetry A_1 (3101 and 3400 cm^{-1}) and two with B_1 (3257 and 3458 cm^{-1}), which subsequently separate into six at 77 K.

As we see in Fig. 2, the frequencies 42 and 75 cm^{-1} of the B_2 and A_1 modes, obtained at room temperature, practically disappear at 77 K. Another anomaly is that the frequency 115 cm^{-1} of the A_1 mode decreases to 111 cm^{-1} at 77 K, instead of increasing as would be expected. We are currently undertaking measurements where the temperature is slowly varied in an attempt to clarify this anomalous behavior.

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