

## INFRARED STUDY OF SULFOHALITE

KEIICHI OMORI, *Institute of Mineralogy, Petrology, and Economic Geology, Tohoku University, Sendai, Japan*

## ABSTRACT

Sulfohalite  $\text{Na}_6\text{FCl}(\text{SO}_4)_2$  is an anhydrous sulfate showing only a small number of infrared absorption bands in the wave number region between 4000 and 60  $\text{cm}^{-1}$ . Sulfohalite was analysed mathematically by factor group analysis on the space group  $O_h^5$  and by site group analysis on  $T_d$  of  $\text{SO}_4$  ion. Force constants of the Urey-Bradley force field are calculated as K 6.45, H 0.70 and F 0.71  $\text{md}/\text{\AA}$  for the  $\text{SO}_4$  ion of sulfohalite. And on the basis of the Urey-Bradley force field, normal vibrations were calculated. All the absorption bands of sulfohalite and also several anhydrous sulfates such as mascagnite, thenardite, glauberite, anhydrite, palmierite, anglesite, barite and celestite can be explained as combination bands. From the absorption bands of sulfohalite found in the far infrared region, the force constants of the octahedral  $\text{FNa}_6$  and  $\text{ClNa}_6$  ions were calculated as K 0.115, H 0.071 and F 0.250  $\text{md}/\text{\AA}$  and K 0.309, H 0.105 and F 0.104  $\text{md}/\text{\AA}$ , respectively and the interaction force constants between the  $\text{FNa}_6$  and  $\text{SO}_4$  ions and also the  $\text{ClNa}_6$  and  $\text{SO}_4$  ions were calculated as  $k$  0.653 and 0.122  $\text{md}/\text{\AA}$ , respectively. The modes of these vibrations are the lattice vibration.

## INTRODUCTION

Sulfohalite  $\text{Na}_6\text{FCl}(\text{SO}_4)_2$  is an anhydrous sulfate with a peculiar isometric form but with symmetry somewhat out of balance. It contains ions of almost similar size including Na, F, Cl, S and O. In the structure, tetrahedral  $\text{SO}_4$  ions are surrounded by 12 Na ions in the cubic face centered lattice, combined with octahedra of NaF and NaCl.

The  $\text{SO}_4$  ion vibrates actively in infrared radiation and shows strong absorption bands, while both octahedra of NaF and NaCl, combined by ionic bonds show no absorption bands.

The infrared absorption of sulfohalite differs from that of mascagnite  $(\text{NH}_4)_2\text{SO}_4$  that shows two kinds of infrared absorption bands, for the  $\text{NH}_4$  ion and  $\text{SO}_4$  ion. Sulfohalite is the anhydrous sulfate with the smallest number infrared absorption bands.

In the present paper the infrared absorption bands of sulfohalite in the wave number region between 4000 and 60  $\text{cm}^{-1}$  are analyzed mathematically.

## SULFOHALITE USED FOR THE STUDY

A crystal of sulfohalite from Searles Lake, California was used for the study. It was powdered in an agate mortar and a KBr disk was made by the usual method (Omori and Kerr, 1964) for infrared study in the wave number region between 4000 and 400  $\text{cm}^{-1}$ . The infrared spectrum obtained by using a Perkin-Elmer Type 125 spectrophotometer with gratings is shown in Figure 1. The band between 900 and 400  $\text{cm}^{-1}$  was also

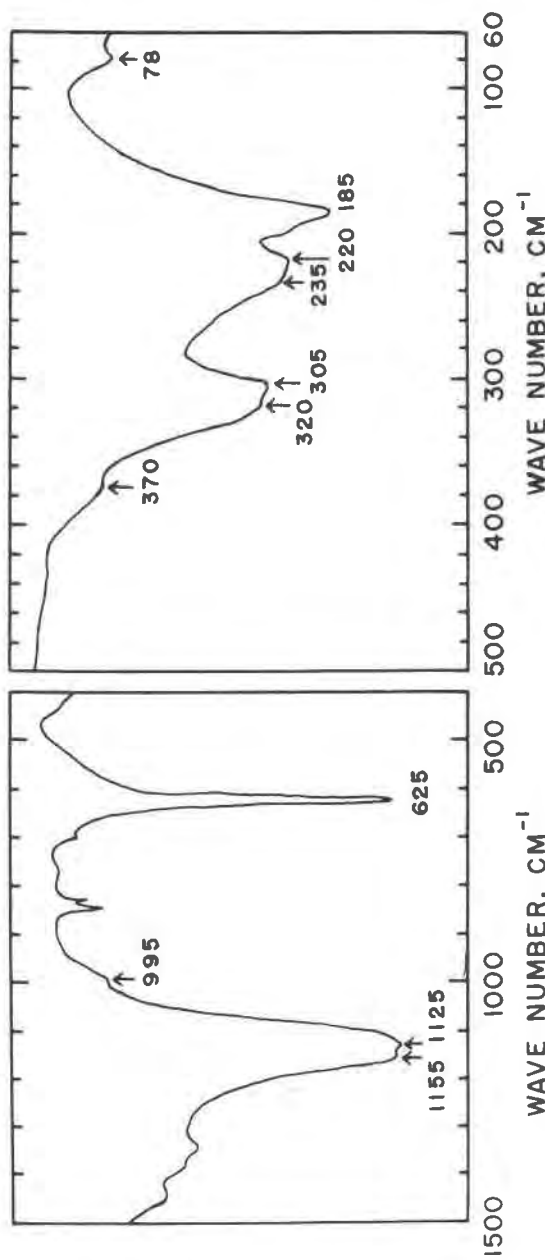


FIG. 1. Infrared absorption spectrum of sulfahalite from Searles Lake, California. Split weak bands at 850 and 830  $\text{cm}^{-1}$  and a weak band at 705  $\text{cm}^{-1}$  are the absorption bands of the  $\text{CO}_3$  ion of a small amount of associated iron  $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

measured accurately by using the Hitachi Type EPI-ST spectrophotometer with a KBr prism.

For the far infrared spectrum the polyethylene plate method was used, with the plate covered by nujol mixed with a small amount of the powdered specimen (Omori, 1968). The far infrared spectrum in the wave number region between 500 and 60  $\text{cm}^{-1}$  was obtained by using the spectrophotometer Hitachi Type FIS-1 with gratings. It is also shown in Figure 1 with the wave numbers of the absorption bands indicated on the spectrum. All wave numbers of the bands are compared in Table 1 between sulfohalite and the free  $\text{SO}_4$  ion.

TABLE 1. INFRARED ABSORPTION BANDS OF SULFOHALITE AND THE FREE  $\text{SO}_4$  ION

Sulfohalite		Free $\text{SO}_4$ ion	
$\nu_{8b}(F_2)$	1155 $\text{cm}^{-1}$	$\nu_3(F_2)$	1104 $\text{cm}^{-1}$
$\nu_{3a}(F_2)$	1125		
$\nu_1(A_1)$	995 (w)	$\nu_1(A_1)$	981 (R)
$\nu_4(F_2)$	625	$\nu_4(F_2)$	613
$\nu_2(E)$	—	$\nu_2(E)$	451 (R)
$\nu_0$	370 (=2×185)		
$\nu_5$	320		
$\nu_7$	305		
$\nu_6$	235		
$\nu_8$	220		
$\nu_9$	185		
$\nu_{10}$	78		

#### FACTOR GROUP ANALYSIS OF SULFOHALITE OF SPACE GROUP $O_h^5$

The crystal structure of sulfohalite has been determined by Watanabe (1934) and Pabst (1934). The space group was considered to be either  $O_h^5-Fm\bar{3}m$  or  $O_h^5-F43$ , cell dimensions given were  $a_0 = 10.15 \text{ \AA}$  (Watanabe) and  $a_0 = 10.08 \text{ \AA}$  (Pabst) and the unit cell contains four molecules of  $\text{Na}_6\text{F} \cdot \text{Cl}(\text{SO}_4)_2$ .

The Bravais unit cell, that is the smallest cell suitable to cover the entire unit cell by translations, contains one molecule of the formula as shown in Figure 2.

As shown in a review by Mitra and Gielisse (1964) a crystal composed of  $N$  cells with  $n$  atoms per cell has  $3Nn$  normal modes of vibration. The  $3Nn$  modes are classified in  $3n$  branches, where  $3n-3$  branches are optical branches and 3 branches are acoustic branches. If the numbers of the normal modes are  $3n-3$ , the numbers  $n$  are the numbers of atoms per Bravais unit cell. The symmetry classification of the vibration can be

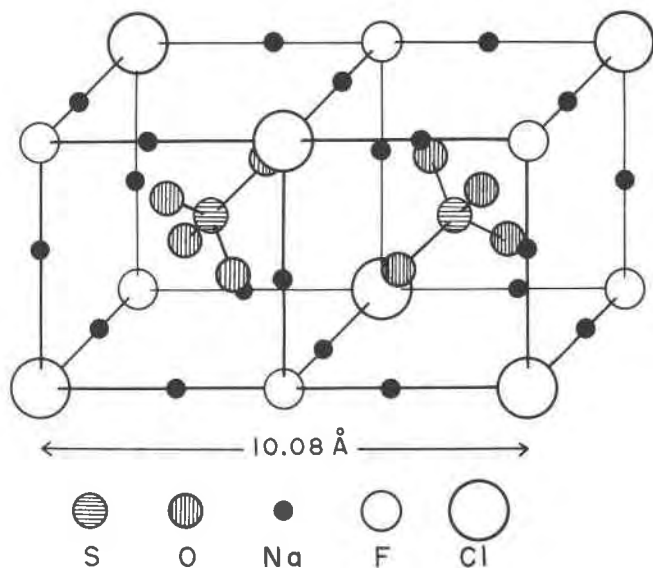


FIG. 2. Bravais unit cell of sulfohalite used for the factor group analysis.

determined by the calculation of factor group analysis on the Bravais unit cell.

Factor group analyses of a number of minerals have been reported. Bhagavantam and Venkatarayudu (1939) have described the Raman effect in relation to the crystal structure and have shown method of factor analysis. Calculated results were shown for diamond, rock salt, calcite and aragonite. Hass and Sutherland (1956) and Tsuboi (1958) have shown the result for gypsum, Mitra (1961) has given the factor group analysis of a crystal containing linear ions such as brucite and liishi, Shiro and Umegaki (1968) have reported the results for corundum and calculated the elastic constants.

The author has performed a factor group analysis of sulfohalite, space group  $O_h^5$ . A character table of the irreducible representations of  $O_h$  used in the calculation is shown in Table 2, where the order of group ( $g$ ) is 48.

The number of times ( $N_k$ ) that a particular irreducible representation ( $\Gamma_k$ ) is contained in another representation ( $\Gamma$ ) can be calculated by the equation

$$N_k = \frac{1}{g} \sum_j h_j \chi_k(R) \chi_j'(R), \quad (1)$$

TABLE 2. FACTOR GROUP ANALYSIS OF SULFOHALITE OF THE SPACE GROUP  $O_h^5$

$O_h^5$ ( $g=48$ )		$I$ $8C_3$ $6C_2$ $6C_4$ $3C_2''$ $i$ $6S_4$ $8S_6$ $3\sigma_h$ $6\sigma_d$	Sulfohalite					$SO_4$ ion					
			$N$	$T$	$T'$	$R'$	$n$	$N$	$T$	$T'$	$R'$	$n$	
$A_{1g}$		1 1 1 1 1 1 1 1 1 1 1	2	0	1	0	1	1	0	0	0	1	
$A_{1u}$		1 1 1 1 1 -1 -1 -1 -1 -1	0	0	0	0	0	0	0	0	0	0	
$A_{2g}$		1 1 -1 -1 1 1 -1 1 1 -1	0	0	0	0	0	0	0	0	0	0	
$A_{2u}$		1 1 -1 -1 1 -1 1 -1 -1 1	1	0	0	0	1	1	0	0	0	1	
$E_g$		2 -1 0 0 2 2 0 -1 2 0	2	0	1	0	1	1	0	0	0	1	
$E_u$		2 -1 0 0 2 -2 0 1 -2 0	1	0	0	0	1	1	0	0	0	1	
$F_{1g}$		3 0 -1 1 -1 3 1 0 -1 -1	2	0	1	1	0	1	0	0	1	0	
$F_{1u}$		3 0 -1 1 -1 -3 -1 0 1 1	7	1	4	0	2	3	1	0	0	2	
$F_{2g}$		3 0 1 -1 -1 3 -1 0 -1 1	4	0	2	0	2	3	0	1	0	2	
$F_{2u}$		3 0 1 -1 -1 -3 1 0 1 -1	2	0	1	1	0	1	0	0	1	0	
Sulfohalite	$U(p)$	18	6	2	4	6	2	4	0	6	10	54	
	$U(s)$	10	4	2	4	6	2	4	0	6	6		30
	$U(s-v)$	2	2	0	0	2	0	2	0	0	2		
	$(N)$	54	0	-2	4	-6	-6	-4	0	6	10		
	$(T)$	3	0	-1	1	-1	-3	-1	0	1	1		
	$(T')$	27	0	-1	3	-5	-3	-3	0	5	5		
$(R')$	6	0	0	0	-2	0	2	0	0	-2			
$SO_4$ ion	$U(p)$	10	4	0	0	2	0	2	0	0	6	30	
	$U(s)$	2	2	0	0	2	0	2	0	0	2		
	$U(s-v)$	2	2	0	0	2	0	2	0	0	2		
	$(N)$	30	0	0	0	-2	0	-2	0	0	6		
	$(T')$	3	0	1	-1	-1	3	-1	0	-1	1		
	$(R')$	6	0	0	0	-2	0	2	0	0	-2		

where  $h_j$  is the number of group operations contained in the  $j$ th class, and  $\chi_k(R)$  and  $\chi_j'(R)$  are the characters of the group operation ( $R$ ) in the representations  $\Gamma_k$  and  $\Gamma$ , respectively.

The group characters  $\chi_j'(R)$  are obtained by the following equations.

The group character  $\chi_j'(N)$  of all unit cell modes in  $3n$  Cartesian coordinates

$$\chi_j'(N) = U(p)(\pm 1 + 2 \cos \phi_R),$$

where  $U(p)$  is the number of atoms remaining invariant under the symmetry operation ( $R$ ) and  $\phi_R$  is the angle of rotation corresponding to the symmetry operation ( $R$ ). The signs plus and minus stand for proper and improper rotations, respectively.

The group character for the acoustic modes is

$$\chi_j'(T) = \pm 1 + 2 \cos \phi_R.$$

When  $U(s)$  is the number of the structural groups remaining invariant under an operation ( $R$ ), the group character of the translatory lattice modes

$$\chi_j'(T') = [U(s) - 1](\pm 1 + 2 \cos \phi_R).$$

Then,  $U(s-v)$  is the number of the polyatomic groups remaining invariant under the operation ( $R$ ), the group character of the rotatory lattice modes

$$\chi_j'(R') = [U(s - v)](1 \pm 2 \cos \phi_R),$$

where  $v$  is the number of the monatomic group and the signs plus and minus stand for proper and improper rotation, respectively.

The characters of sulfahalite and the  $\text{SO}_4$  ion are shown in the fifth and sixth broad columns in Table 2, while the classified numbers of the modes of vibration are shown in the third and fourth broad rows in Table 2.

The total number of lattice vibrations is obtained as the sum of  $T'$  and  $R'$  and the number of the molecular vibrations is obtained from the subtraction

$$n = N - T - T' - R'.$$

Although the symmetry species  $F_{1u}$  belongs to the infrared active species, combinations exist between  $F_{1u}$  and  $F_{2g}$ , thus the numbers ( $n$ ) of the molecular vibration of the  $\text{SO}_4$  ion are found as two, and the numbers of the lattice vibration of sulfahalite are six from the sum of the numbers ( $T'$ ) in  $F_{1u}$  and  $F_{2g}$ . The numbers calculated are similar to the numbers of the band obtained on the infrared spectrum.

#### SITE GROUP ANALYSIS

In the classified description (Bragg, Laue, Hermann *et al.* 1935) of the space group,  $O_h^5$  has a subgroup  $T_d$ , and  $O^3$  has no subgroup  $T_d$ , thus the tetrahedral  $\text{SO}_4$  ion contained in  $O_h^5$  belongs to the site group  $T_d$ .

The total number of the normal modes of vibration of the  $\text{SO}_4$  ion is calculated as nine ( $3 \times 5 - 6 = 9$ ). The nine degrees of freedom are classified as  $A_1 + E + 2F_2$  by calculations using the character table of the irreducible representation of  $T_d$  and the equation (1). It is given from the calculation of the selection rules that the infrared active vibrational modes are  $2F_2$ .

When the  $\text{SO}_4$  ion belongs to the point group  $C_{3v}$ , the total modes of vibration are  $3A_1 + 3E$ , where the infrared active modes are  $3A_1 + 3E$ . When it belongs to the point group  $C_{2v}$ ,  $C_2$  and  $S_4$ , the infrared active mode is  $4A_1 + 2B_1 + 2B_2$ ,  $5A + 4B$  and  $3B + 2E$ , respectively.

There are differences between the numbers of the infrared active modes of  $T_d$ ,  $C_{3v}$ ,  $C_{2v}$ ,  $C_2$  and  $S_4$ . Since the point group  $T_d$  belongs to the space group  $O_h^5$ , although there are two bands of  $\nu_3$  on the spectrum of

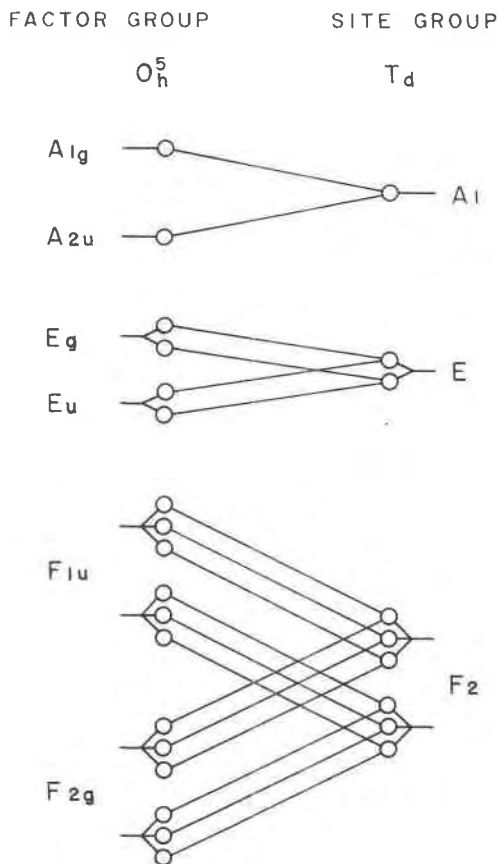


FIG. 3. Correlation chart of the normal modes of vibration of the  $SO_4$  ion between  $O_h^5$  and  $T_d$ .

sulfohalite, it may be considered that the tetrahedral  $SO_4$  ion is in the site group  $T_d$  and the splitting of the stretching  $\nu_3$  band appears owing to the combinations of the vibrational modes. And  $F_{1u}$  and  $F_{2g}$  species in  $O_h^5$  are correlated with the  $F_2$  species in  $T_d$  from the correlation chart shown in Figure 3.

Molecular vibrations of the  $SO_4$  ion appear partially in the crystal lattice, while the lattice vibrations can propagate through the entire crystal lattice. Combinations of these two kinds of vibration cause the splitting of the band and it is considered that the force constants of the  $SO_4$  ion of sulfohalite differ somewhat from these of the free  $SO_4$  ion.

FORCE CONSTANTS OF THE TETRAHEDRAL  $\text{SO}_4$   
ION OF SULFOHALITE

Urey and Bradley (1931) have calculated the vibrational frequencies of tetrahedral molecules such as the  $\text{CCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{CBr}_4$ ,  $\text{SnBr}_4$ ,  $\text{ClO}_4$  and  $\text{SO}_4$  ions under an assumption that the restoring forces can be best chosen as harmonic restoring forces along the directions of the chemical bonds and perpendicular to them. There are two possible cases of forming the  $\text{SO}_4$  ion from  $\text{S}^{6+}$  and  $4\text{O}^{2-}$  and from  $\text{S}^{2+}$  and  $4\text{O}^{1-}$ , and in the latter case the  $\text{SO}_4$  ion is believed to be tetrahedral, but the actual ion may be a combination of both of these and perhaps of other configurations. It was also reported that the inverse repulsive force is in need of the additional term of the electronic charge.

Shimanouti (1949) has calculated the normal modes of vibration as treated by the Urey-Bradley force field, and Decius (1948) has reported a useful tabulation of general formulae for inverse kinetic energy matrix elements in an acyclic molecule. Recently Colthup, Daly and Wiberley (1964) reported a systematic method to calculate the normal modes of vibration of the molecule and described in detail an example,  $\text{CHCl}_3$ .

The author has calculated the force constants of the Urey-Bradley force field for the  $\text{SO}_4$  ion of sulfohalite from the GF matrices using Decius' table of the kinetic energy matrix. The force constants obtained are  $K(\text{S-O})$  6.45,  $H(\text{O-S-O})$  0.70 and  $F(\text{O} \cdots \text{O})$  0.71 md/Å. The force constants of the free  $\text{SO}_4$  ion are already reported as  $K$  6.01,  $H$  0.43 and  $F$  0.76 md/Å.

From the comparison of the force constants of the  $\text{SO}_4$  ion between sulfohalite and the free  $\text{SO}_4$  ion, it is known that the stretching force constant ( $K$ ) and the bending force constant ( $H$ ) of sulfohalite are larger and the repulsive force constant ( $F$ ) is smaller than the force constant of the free  $\text{SO}_4$  ion.

By using the force constants the wave numbers of the normal vibrations were calculated as  $\nu_1$  995,  $\nu_3$  1142 and  $\nu_4$  625  $\text{cm}^{-1}$ , all of which are near similar to the wave numbers measured.

## COMBINATION BANDS OF SULFOHALITE

Combination bands appear because of the direct interactions between the infrared radiation and the phonons in the crystal lattice. And a phonon is absorbed and through the state where the normal mode of vibration is excited, two phonons are created. The combination bands exist where a phonon is absorbed and two or more phonons are emitted.

The infrared absorption bands of sulfohalite are attributed to the combination bands. The summation of each band is examined and the results obtained shown below.



The  $\nu_{3b}$  band ( $1155 \text{ cm}^{-1}$ ):

$$\left. \begin{aligned} \nu_4 + \nu_5 + \nu_8 &= 1165 \text{ cm}^{-1} \\ \nu_4 + \nu_7 + \nu_8 &= 1140 \\ \nu_4 + \nu_6 + \nu_8 + \nu_{10} &= 1158 \\ \nu_5 + \nu_7 + \nu_6 + \nu_8 + \nu_{10} &= 1158 \end{aligned} \right\} \text{Mean } 1155 \text{ cm}^{-1}$$

Since  $\nu_4 = \nu_5 + \nu_7$ ,

$$\nu_{3b} = \frac{1}{4}[5(\nu_5 + \nu_7) + 2(\nu_6 + 2\nu_8 + \nu_{10})].$$

The  $\nu_{3a}$  band ( $1125 \text{ cm}^{-1}$ ):

$$\left. \begin{aligned} \nu_4 + \nu_5 + \nu_9 &= 1130 \text{ cm}^{-1} \\ \nu_4 + \nu_7 + \nu_9 &= 1115 \\ \nu_4 + \nu_6 + \nu_9 + \nu_{10} &= 1123 \\ \nu_5 + \nu_7 + \nu_6 + \nu_9 + \nu_{10} &= 1123 \end{aligned} \right\} \text{Mean } 1123 \text{ cm}^{-1}$$

Since  $\nu_4 = \nu_5 + \nu_7$ ,

$$\nu_{3a} = \frac{1}{4}[5(\nu_5 + \nu_7) + 2(\nu_6 + 2\nu_9 + \nu_{10})].$$

The splitting of  $\nu_{3b}$  and  $\nu_{3a}$  of  $F_2$  mode is due to the variation between the absorption band  $\nu_8$  and  $\nu_9$ .

The summation of band  $\nu_3$  ( $981 \text{ cm}^{-1}$ ) of the free  $\text{SO}_4$  ion

$$\nu_3 = 2\nu_5 + \nu_8 + \nu_9 + \nu_{10} = 1104 \text{ cm}^{-1}.$$

Variations of the bands between  $\nu_5$  and  $\nu_7$ , between  $\nu_6$  and  $\nu_8$  and between  $\nu_8$  and  $\nu_9$  are considered to originate the band variations between  $\nu_{3b}$ ,  $\nu_{3a}$  and  $\nu_3$ .

The  $\nu_4$  band ( $625 \text{ cm}^{-1}$ ):

$$\nu_4 = \nu_5 + \nu_7 = 625 \text{ cm}^{-1}$$

The summation of  $\nu_4$  band ( $613 \text{ cm}^{-1}$ ) for the free  $\text{SO}_4$  ion

$$\nu_4 = 2(\nu_8 + \nu_{10}) = 596 \text{ cm}^{-1}.$$

The  $\nu_4$  band of sulfohalite is due to the variation between  $\nu_5$  and  $\nu_6$ , where  $\nu_7 = \nu_8 + \nu_{10}$ .

The  $\nu_1$  band ( $995 \text{ cm}^{-1}$ ):

This is an apparent band in the infrared spectrum.

$$\nu_1 = \nu_4 + \nu_0 = 995 \text{ cm}^{-1}$$

The  $\nu_1$  band ( $981 \text{ cm}^{-1}$ ) of the free  $\text{SO}_4$  ion has the following combination.

$$\nu_1 = 2\nu_0 + \nu_8 = 980 \text{ cm}^{-1}$$

And  $\nu_2$  band ( $450 \text{ cm}^{-1}$ ) of the free  $\text{SO}_4$  ion is the combination band as

$$\nu_2 = \nu_0 + \nu_{10} = 448 \text{ cm}^{-1}.$$

The  $\nu_0$  band ( $370 \text{ cm}^{-1}$ ) is an overtone of the  $\nu_9$  band,

$$\nu_0 = 2\nu_9 = 370 \text{ cm}^{-1}.$$

And the differences between  $\nu_5$  and  $\nu_7$  and between  $\nu_6$  and  $\nu_8$  are similar.

$$\nu_5 - \nu_7 = 15 \text{ cm}^{-1}$$

$$\nu_6 - \nu_8 = 15$$

Similar combinations of bands are also found in other anhydrous sulfates. The examples are shown in Table 3, where all the wave numbers of absorption bands have been measured by the author on the spectra shown in Figure 4. The inner molecular vibrations vibrate partially in the crystal lattice and vibrate in harmony with the vibrations in the far infrared region, which propagate in the entire crystal lattice. The splitting of the absorption bands and the vibration of the wave number are attributed to the different combinations of the characteristic phonons.

#### ABSORPTION BANDS IN THE FAR INFRARED REGION

Although seven absorption bands are found in the far infrared region of the spectrum of sulfohalite, the  $\nu_0$  band at  $370 \text{ cm}^{-1}$  seems to be an overtone of the  $\nu_9$  band at  $185 \text{ cm}^{-1}$ .

The octahedral ions,  $\text{FNa}_6$  and  $\text{ClNa}_6$ , are found in the crystal structure of sulfohalite. The force constants, K, H and F, of the octahedral ions were calculated by using the GF matrices. The force constants obtained and the wave numbers calculated are shown below.

Octahedral  $\text{FNa}_6$  ion:  $K = 0.115$ ,  $H = 0.071$  and  $F = 0.250 \text{ md}/\text{\AA}$

Wave numbers measured 320( $\nu_5$ ) and 235( $\nu_6$ )

Wave numbers calculated 321                      242

Octahedral  $\text{ClNa}_6$  ion:  $K = 0.309$ ,  $H = 0.105$  and  $F = 0.104 \text{ md}/\text{\AA}$

Wave numbers measured 305( $\nu_7$ ) and 220( $\nu_8$ )

Wave numbers calculated 305                      202.

Then, the force constant  $k$  of the interaction between the  $(\text{F,Cl})\text{Na}_6$  and  $\text{SO}_4$  ions was calculated by using the following equation

$$\lambda = \frac{4}{3} k [2\mu_{((\text{F,Cl})\text{Na}_6)} + \mu_{(\text{SO}_4)}],$$

TABLE 3. COMBINATIONS OF THE INFRARED ABSORPTION BANDS OF ANHYDROUS SULFATES

1. Mascagnite		595 ... 283+191+120 = 594
( $\nu_1$ )	970 (w) 450+220×2+80 = 970 cm <sup>-1</sup>	283+173+140 = 596
( $\nu_2$ )	450 (w) 220×2 = 440	( $\nu_2$ ) 510 ... 191+173+140 = 504
	380+80 = 460	283 ... 173+105 = 278
2. Sulfohalite		140×2 = 280
( $\nu_3$ )	1155 ... 625+320+220 = 1165	238 ... 140+105 = 245
	625+305+220 = 1140	120×2 = 240
	625+235+220+78 = 1158	
	320+305+235+220+78 = 1158	
	1125 ... 625+320+185 = 1130	
	625+305+185 = 1115	
	625+235+185+78 = 1123	
	320+305+235+185+78 = 1123	
( $\nu_1$ )	995 (w) 625+370 = 995	
( $\nu_4$ )	625 ... 320+305 = 625	
	370 ... 185×2 = 370	
3. Thenardite		
( $\nu_3$ )	1155(sh) 1010+145 = 1155	
	1120 ... 617+180×2+145 = 1122	
( $\nu_1$ )	1010 ... 617+180+145+75 = 1017	
( $\nu_4$ )	633 ... 450+180 = 630	
	617 ... 180+145×2+75×2 = 620	
( $\nu_2$ )	450 ... 145×2+75×2 = 440	
	145 ... 75×2 = 150	
4. Glauberite		
( $\nu_3$ )	1140 ... 995+135 = 1130	
	1105 ... 645+464 = 1109	
	630+475 = 1105	
( $\nu_1$ )	995 ... 475+288+230 = 993	
( $\nu_4$ )	645 ... 464+186 = 650	
	288+230+135 = 653	
	609 ... 288+186+135 = 609	
( $\nu_2$ )	475 ... 288+186 = 474	
	464 (w) 230×2 = 460	
5. Anhydrite		
( $\nu_3$ )	1190(sh) 595×2 = 1190	
	675+510 = 1185	
	675+283+238 = 1196	
	612+283+191+105 = 1191	
1153 ...	675+283+191 = 1149	
	675+191+173+120 = 1159	
	612+238+191+105 = 1146	
	595+283+173+105 = 1156	
	595+238+173+140 = 1146	
1119 ...	675+191+140+120 = 1126	
	612+238+140+120 = 1110	
	595+283+238 = 1116	
	595+283+140+105 = 1123	
	595+238+173+120 = 1126	
( $\nu_4$ )	675 ... 510+173 = 683	
	238+191+140+105 = 674	
	238+173+140+120 = 671	
612 ...	510+105 = 615	
	283+191+140 = 614	
6. Palmierite		
( $\nu_3$ )	1190 ... 990+190 = 1180	
	650+343+190 = 1183	
	615+295+166+105 = 1181	
1140 ...	650+295+190 = 1135	
	615+343+190 = 1148	
1105 ...	650+343+105 = 1098	
	635+475 = 1110	
	615+295+190 = 1100	
( $\nu_1$ )	990 ... 650+343 = 993	
	343+295+190+166 = 994	
( $\nu_4$ )	650 (w) 295+190+166 = 651	
	635(sh) 343+295 = 638	
	615 ... 343+166+105 = 614	
( $\nu_2$ )	475 ... 295+190 = 483	
	445 ... 343+105 = 448	
	295 ... 190+105 = 295	
7. Anglesite		
( $\nu_3$ )	1105 ... 592+185+150+104+73 = 1109	
	960+150 = 1110	
	1165 ... 960+185 = 1145	
	1045 ... 592+185+150+120 = 1047	
( $\nu_1$ )	960 ... 620+150+120+73 = 963	
	592+150+120+104 = 966	
( $\nu_4$ )	620 ... 185+150+120+104+73 = 632	
8. Barite		
( $\nu_3$ )	1120 ... 608+198+167+142 = 1115	
	980+142 = 1122	
	1180 ... 980+198 = 1178	
	1080 ... 633+167+142+125 = 1087	
	608+198+142+125 = 1073	
( $\nu_1$ )	980 ... 633+198+142 = 973	
	608+198+167 = 973	
	608+142+125+100 = 975	
( $\nu_4$ )	633 ... 198+167+142+125 = 632	
	608 ... 198+167+142+100 = 607	
9. Celestite		
( $\nu_3$ )	1130 ... 610+212+170+132 = 1124	
	990+132 = 1122	
	1195 ... 990+212 = 1202	
	1095 ... 639+212+132+120 = 1103	
	610+212+147+120 = 1089	
( $\nu_1$ )	990 ... 639+212+147 = 998	
	610+212+170 = 992	
( $\nu_4$ )	639 ... 212+170+132+120 = 634	
	610 ... 212+147+132+120 = 611	

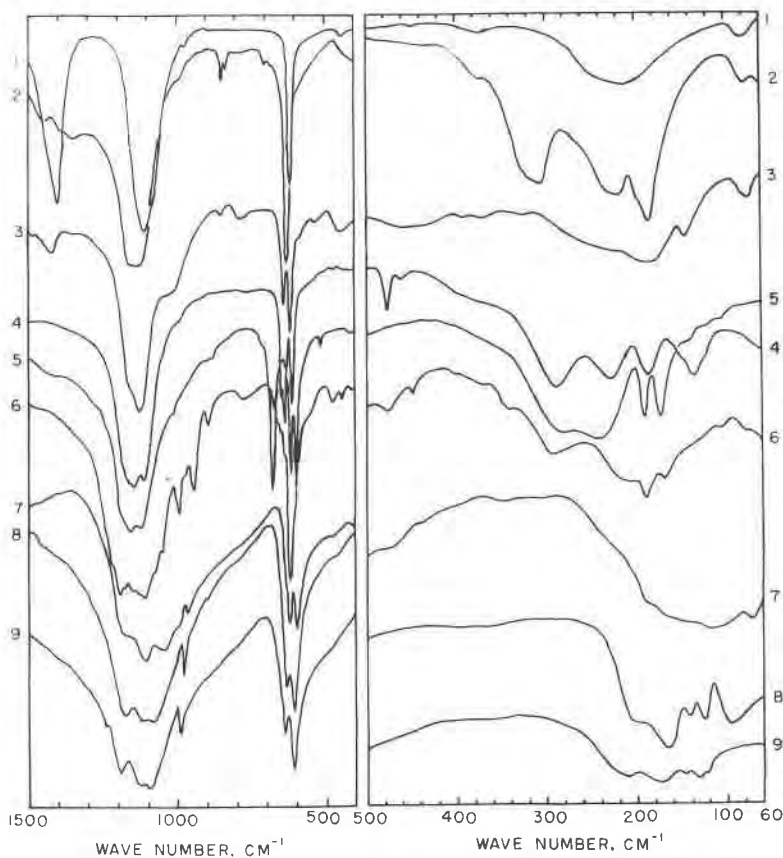


FIG. 4. Infrared absorption spectra of the anhydrous sulfates in the wave number region between 1500 and 60  $\text{cm}^{-1}$ . 1. Mascagnite, Larderello, Tuscany, Italy, 2. Sulfohalite, Searles Lake, Calif., 3. Thenardite, Borax Lake, Lake Co., Calif., 4. Glauberite, San Bernardino Co., Calif., 5. Anhydrite, Roundhouse, Nev., 6. Palmierite, Vesuvius, Italy, 7. Anglesite, Los Lamentos, Chihuahua, Mexico, 8. Barite, Tazewell Co., Va., and 9. Celestite, Strontian Island, Lake Erie.

where  $\mu_{((F,Cl)Na_6)}$  is the reciprocal mass of either  $FN_{a_6}$  or  $ClNa_6$  ion and  $\mu_{(SO_4)}$  is the reciprocal mass of the  $SO_4$  ion. The interaction force constants obtained are  $k$  0.653  $\text{md}/\text{\AA}$  for the  $FN_{a_6}$  and  $SO_4$  ions from the absorption band at 185  $\text{cm}^{-1}$  ( $\nu_9$ ) and  $k$  0.122  $\text{md}/\text{\AA}$  for the  $ClNa_6$  and  $SO_4$  ions from the absorption band at 78  $\text{cm}^{-1}$  ( $\nu_{10}$ ). The modes of these vibrations are the lattice vibration.

#### CONCLUSIONS

Infrared and the far infrared absorption spectra of sulfohalite  $Na_6FCl(SO_4)_2$  were studied and in addition mascagnite  $(NH_4)_2SO_4$ ,

thenardite  $\text{Na}_2\text{SO}_4$ , glauberite  $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ , anhydrite  $\text{CaSO}_4$ , palmierite  $(\text{K},\text{Na})_2\text{Pb}(\text{SO}_4)_2$ , anglesite  $\text{PbSO}_4$ , barite  $\text{BaSO}_4$  and celestite  $\text{SrSO}_4$  in the wave number region between 4000 and 60  $\text{cm}^{-1}$ .

The single sulfate that contains one ion of  $\text{SO}_4$  in its chemical formula is orthorhombic dipyramidal, while the double sulfate that contains two ions of  $\text{SO}_4$  in its chemical formula is either monoclinic prismatic or rhombohedral scalenohedral. Sulfate containing holoogens such as sulfohalite is isometric, such as schairerite is rhombohedral or such as chlorothionite is orthorhombic.

Among the anhydrous sulfates sulfohalite shows a small number of infrared absorption band from 4000  $\text{cm}^{-1}$  to 60  $\text{cm}^{-1}$ . Though the absorption of mascagnite is also the small number, the bands of the  $\text{SO}_4$  ion are accompanied by the bands of  $\text{NH}_4$  ion.

Factor group analysis of sulfohalite for  $O_h^5$  is shown in Table 2. Site group analysis of the  $\text{SO}_4$  ion of  $T_d$  shows that the infrared active modes are two  $F_2$  shown in Figure 3.

Force constants of the Urey-Bradley force field are calculated  $K(\text{S-O})$  6.45,  $H(\text{O-S-O})$  0.70 and  $F(\text{O} \cdots \text{O})$  0.71  $\text{md}/\text{\AA}$  for the  $\text{SO}_4$  ion of sulfohalite. The stretching force constant (K) and the bending force constant (H) of sulfohalite are larger and the repulsive force constant (F) is smaller than those of the free  $\text{SO}_4$  ion.

From the analyses of the absorption bands in the far infrared region the force constants K 0.115, H 0.071 and F 0.250  $\text{md}/\text{\AA}$  for the octahedral  $\text{FNa}_6$  ion and K 0.309, H 0.105 and F 0.104  $\text{md}/\text{\AA}$  for the octahedral  $\text{ClNa}_6$  ion were obtained. And the interaction force constants k 0.653 and 0.122  $\text{md}/\text{\AA}$  were calculated for the  $\text{FNa}_6$  and  $\text{SO}_4$  ions and the  $\text{ClNa}_6$  and  $\text{SO}_4$  ions, respectively. The mode of these vibrations is the lattice vibration.

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