INTERPRETATION OF RAMAN SPECTRA IN CRYSTALS: ANHYDRITE AND GYPSUM.

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1. Introduction.

THE application of group theory to a study of the normal modes of oscillation of crystal lattices with special reference to Raman scattering has yielded very fruitful results. A comprehensive account will be published separately. The two interesting cases of anhydrite ($CaSO_4$) and gypsum ($CaSO_4 \cdot 2\,H_2O$) are dealt with in the present paper. The fact that the crystal structures as well as the Raman spectra of both these substances have been studied in considerable detail is of great help in this connection.

2. Crystal Structure.

The crystal lattice of anhydrite is an ionic one. The crystals belong to the orthorhombic variety and the space group is V_h^{17}. The unit cell contains four molecules. The structure of gypsum is also ionic and the unit cell which belongs to the monoclinic class contains again four molecules. The space group is C_{2h}^3. Attempts have been made to fix the atomic positions in both these cases from the results of X-ray analysis and it is believed that the SO_4 ions preserve their tetrahedral symmetry in the crystalline state also. In the present paper, we will consider the anhydrite crystal as consisting of Ca and SO_4 groups and gyspum as consisting of $Ca \cdot 2\,H_2O$ and SO_4 groups. Further details in respect of these well-known structures may be obtained from Wyckoff.[1]

3. Raman Spectra.

The Raman spectra of anhydrite and gypsum have been studied by a number of investigators. Complete references are to be found in Landolt Bornstein Tabellen. The frequencies given below are taken from these Tables :

TABLE I. *Raman Frequencies.*

Substance	Lattice	Internal to SO_4 ion				Water bands
SO_4 ion ..	..	454 (ν_2) double	622 (ν_3) triple	983 (ν_1) single	1106 (ν_4) triple	..
$CaSO_4$ (Anhydrite)	126 169 233 (1) (2) (1)	415 499 (1) (5d)	609 628 674 (2) (2) (8)	1018 (15)	1108 1128 1160 (2) (10) (5)	..
$CaSO_4 \cdot 2H_2O$ (gypsum)	..	414 494 (5) (3)	.. 618 672 (2b) (4)	1008 (20)	1113 1135 .. (2) (10)	3402 3493 (10d) (20)

[1] *The Structure of Crystals*, 2nd Edn., 1931.

The case of the free SO_4 ion is also included for comparison. The frequencies have been divided into various classes, the division being self-explanatory. The degree of degeneracy and the conventional designation is indicated in each case for the frequencies of the free ion. As the corresponding modes are well known, they need not be described here in detail. The splitting in the crystalline state of all the degenerate frequencies belonging to the tetrahedral SO_4 ion is noteworthy. This result has been described by Nisi[2] as being inconsistent with the X-ray evidence and was taken to indicate a departure from the tetrahedral symmetry for the SO_4 ions in the crystalline state. The present investigation on the contrary, shows clearly that the splitting is to be expected since the crystal as a whole does not possess the high degree of symmetry that is characteristic of the SO_4 ion. The result is therefore not inconsistent with the view that the SO_4 ions preserve their tetrahedral symmetry in the crystalline state.

4. Symmetry Properties and Character Tables.

TABLE II.

Anhydrite.

V_h	E	C^1	C_2	C_2'	i	σ_h	σ_v	σ_v'	n_j	External		n_j'	Raman	Infra-red
										T	L			
A_{1g}	1	1	1	1	1	1	1	1	12	0	4	8	p	f
A_{2g}	1	−1	1	−1	1	−1	1	−1	10	0	6	4	p	f
B_{1g}	1	1	−1	−1	1	1	−1	−1	4	0	2	2	p	f
B_{2g}	1	−1	−1	1	1	−1	−1	1	10	0	6	4	p	f
A_{1u}	1	1	1	1	−1	−1	−1	−1	4	0	2	2	f	f
A_{2u}	1	−1	1	−1	−1	1	−1	1	10	1	5	4	f	p
B_{1u}	1	1	−1	−1	−1	−1	1	1	12	1	3	8	f	p
B_{2u}	1	−1	−1	1	−1	1	1	−1	10	1	5	4	f	p
U_r	24	8	0	0	0	0	16	16						
$h_j \chi_j'$	72	−8	0	0	0	0	16	16						

[2] Proc. Phys. Math. Soc., Japan, 1933, 15, 463.

TABLE III.

Gypsum.

C_{2h}	E	C_2	i	σ	n_i	External		n_i'	Raman	Infra-red
						T	L			
A_1 ..	1	1	1	1	1;	0	6	10	p	f
A_2 ..	1	−1	1	−1	20	0	12	8	p	f
B_1 ..	1	1	−1	−1	16	1	5	10	f	p'
B_2 ..	1	−1	−1	1	20	2	10	8	f	p
U_r ..	24	8	0	0						
$h_j \chi_j'$	72	−8	0	0						

The notation is the same as that employed in earlier papers published in these *Proceedings*. n_j' represents the number of oscillations that are internal to the SO_4 group. p and f under the columns Raman and infra-red indicate respectively that the line is permitted or forbidden from appearing. We will first consider the internal oscillations n_j'. A very complete analysis of all the normal modes appropriate to the unit cell[3] has been made with a view to understand the significance of the splitting in each case. The details will not be given here, but we will state the results. In each crystal there are 36 internal oscillations. The four distinct modes of oscillation appropriate to the free SO_4 group split into nine distinct modes in the crystal as the degeneracy disappears on account of its lower symmetry. These nine distinct modes undergo a further splitting on account of the fact that there are four such groups in each unit cell, thus giving an aggregate of 36 modes. The former splitting may be expected to be more prominent than the latter. Detailed analysis shows that one or other of the four components coming from each one of the nine fundamental modes falls in the Raman active class and we should accordingly expect both anhydrite and gypsum to exhibit all the nine components in their respective Raman spectra. As these components are only slight modifications of the original modes, we may further expect a close correspondence between the split frequencies in the crystal and those of the free ion. The results in respect of the internal oscillations given in Table I completely support this view. The correspondence between

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[3] These modes when extended to an infinite lattice will correspond to the limiting frequencies of the various optical series in the notation of Born and Karman. The pure translations given under T constitute the acoustic series.

the degenerate frequencies of the free SO_4 ion and the split components in the crystal is evident. The results in respect of gypsum suggest that one faint line in the neighbourhood of 600 and another in the neighbourhood of 1160 are yet to be recorded.

The experimental results in respect of the lattice oscillations are by no means definite. Many weak lines reported by different investigators have been omitted from Table I as their reality is somewhat uncertain. The investigations described in the present paper show that several more lattice frequencies are to be expected than those contained in Table I. In fact the figures given in Landolt but not included here show that the low frequency spectrum of gypsum is quite complex. A more complete experimental investigation of these low frequencies is obviously necessary. The water bands present a problem by themselves and will be dealt with separately.

5. Summary and Conculsion.

Application of group theory to a study of the normal oscillations of the crystal lattices of anhydrite and gypsum shows that we should expect the degenerate modes of the free SO_4 ion to completely split up in the crystal. All the split components are Raman active. The experimental results obtained with anhydrite are in enitre agreement with this view. The case of gypsum also gives results which are in general agreement with the theory. The splitting is a consequence of the lower symmetry of the crystals as a whole and need not be taken as indicating a lack of tetrahedral symmetry for the SO_4 ions individually.