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THE SECOND ORDER RAMAN SPECTRUM OF CALCIUM FLUORIDE

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Résumé. — Les auteurs discutent, d'après les théories actuelles de la dynamique des cristaux, le spectre Raman de second ordre du fluorure de calcium enregistré récemment par Russell au moyen d'un laser He-Ne (1). Ce spectre est examiné en détail, avec calcul des fréquences des modes des super mailles d'après les modèles dynamiques de Ramanathan et de Ganesan et Srinivasan, en appliquant les règles de sélection à la combinaison des points critiques X pour les structures CaF_2. On explique de façon satisfaisante la plupart des déplacements de fréquences du second ordre observés.

Abstract. — The second-order Raman spectrum of calcium fluoride recorded recently by Russell, using a He-Ne laser source, is discussed in the light of current theories on the dynamics of crystals. The observed spectrum of CaF_2 is examined in detail with a calculation of the frequencies of the supercell modes using the lattice dynamic models of Ramanathan and Ganesan and Srinivasan, with the selection rules for the combinations from the critical points X for CaF_2 structures. Satisfactory explanations have been given for most of the observed second-order frequency shifts.

1. **Introduction.** — The first order Raman spectrum of calcium fluoride consists of only a single Raman line with the frequency shift of 322 cm^{-1} [1] Recently, the second order Raman spectrum of calcium fluoride has been recorded by Russell [2] using the intense monochromatic light beam at λ 6 328 Å available from a He-Ne laser. The dynamics of the calcium fluoride lattice in the Raman theory has already been worked out by Ramanathan [3]. The conventional lattice dynamical calculations based on the Born dynamics has been carried out by Ganesan and Srinivasan [4] using two different models to explain the diffuse X-ray scattering and the thermal properties. The phonon branches from the critical points have been worked out for all the three models and an assignment of the observed second-order spectrum is attempted. Selection rules governing the combinations from the critical point X, in particular, have been worked out to facilitate the assignments.

2. **Discussion.** — Recent studies on the second-order Raman spectra of alkali-halides and diamond have clearly shown the inadequacy of the quasi-continuous frequency distributions alone to explain satisfactorily the sharp peaks or lines observed in these cubic diatomic crystals. The appea-

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(1) Voir communication de Russell au présent Colloque.

rance of these Raman lines can be accounted for by the Van Hove singularities in the frequency distribution function [5]. It has been pointed out by us [6] that in the case of cubic crystals the critical points at L and X give rise to phonon frequencies which correspond to the vibrations of the planes of atoms like the (111) or (100) which are nothing but the modes of the supercell pictured in the Raman theory [7]. In the preceding paper the present authors [8] have satisfactorily explained most of the second-order Raman lines in the case of gallium phosphide by applying the Raman theory. The same procedure has now been adopted to account for the special features of the second-order Raman spectrum of calcium fluoride.

The fluorite structure has three interpenetrating face-centred cubic lattices instead of two and hence it has 72 degrees of freedom for the Raman supercell and these modes of vibration may be derived from those of a face-centred cubic lattice by considering the three possible alternatives: (1) the Ca and the two F ions are all in the same phase of vibration, (2) the Ca is in one phase and F ions in the opposite phase (3) the two F ions move in opposite phases, the Ca ions remain at rest. These three alternatives thus constitute the acoustic, Raman and infrared branches of the vibration spectrum in the conventional Born dynamics. In the octahedral planes, the Ca and F ions appear in distinct layers at unequal intervals, each Ca having

TABLE I

VIBRATION SPECTRUM OF CALCIUM FLUORIDE

DESIGNATION	DESCRIPTION	DEGENERACY	$4\pi^2 c^2 \nu^2 m_h$	RAMANATHAN'S MODEL	GANESAN AND SRINIVASAN	
					MODEL I	MODEL II
—	—	—	—	—	—	—
ν_1 (Γ)	Vibrations of the fluorine lattices against each other, calcium atoms at rest.	3	$(P_2 - 2T_2 + 8V)/m_2$	254 463	254 463	254 463
ν_2 (Γ)	Vibrations of the calcium lattice against the F_2 lattice as a whole.	3	$\left(\frac{P_1 + 8T_1}{m_1} + \frac{P_2 + 2T_2 + 8V}{m_2}\right) = -4Q\left(\frac{2}{m_1} + \frac{1}{m_2}\right)$	322	322	322
ν_3 (X)	Vibrations of the calcium atoms normal to the cube planes.	3	$P_1 - 8T_1/m_1$	331	334	329
ν_4 (X)	Coupled vibrations of the two fluorine lattices normal to the cube planes. Ca atoms at rest.	3	$P_2 - 2T_2 - 8V/m_2$	459	456	404
ν_5 (X)		3	P_2/m_2	349	231	157
ν_6 (X)	Vibration of Ca atoms tangential to the cube planes, F atoms at rest.	6	P_1/m_1	265	224	238
ν_7 (X)	Coupled vibrations of F atoms tangential. To cube planes, Ca atoms at rest.	6	$P_2 + 2T_2/m_2$	295	239	351
ν_8 (X)		6	$P_2 + 2T_2 + 4V/m_2$	245	153	166
ν_9 (L)	Vibrations of the fluorine lattices normal to octahedral planes.	4	$P_2 - 8V/m_2$	419	355	320
ν_{10} (L)	Coupled vibrations of Ca and F atoms normal to octahedral planes.	4	$\left(\frac{7/8\,P_1 - 3T_1}{m_1}\right) + \left(\frac{3/4\,P_2 - 3V + 1/4\,T_2}{m_2}\right)$	428	442	328
ν_{11} (L)		4	$\left(\frac{1/8\,P_1 - 5T_1}{m_1}\right) + \left(\frac{1/4\,P_2 - 5V - 1/4\,T_2}{m_2}\right)$	303	267	311
ν_{12} (L)	Vibrations of F atoms tangential to octahedral planes.	8	$P_2 + 4V/m_2$	308	265	267
ν_{13} (L)	Coupled vibrations of Ca and F atoms tangential to octahedral planes.	8	$\left(\frac{P_1 + 6T_1}{m_1}\right) + \left(\frac{P_2 + T_2 + 6V}{m_2}\right)$	325	289	317
ν_{14} (L)		8	$-\left(\frac{2T_1}{m_1} + \frac{2V + T_2}{m_2}\right)$	202	156	150

two F layers disposed symmetrically on either side; on the other hand, in the cubic planes, the atoms appear in equidistant layers, the Ca and F ions jointly occupying the alternate layers.

The modes of the Raman supercell for CaF_2 structure are described in Table I with the respective degeneracies. From the above description, it is evident that they correspond to the critical point phonon branches from Γ, L and X. The three fold and six fold or four fold and eight fold degeneracies associated with the supercell modes involving the longitudinal or transverse oscillations of the cubic or octahedral planes correspond to the phonon branches from the three equivalent X points or four L points. A subdivision into optical and acoustic branches can be given with the help of the phase relations. Thus we see that for the CaF_2 structure, the 72 modes can be explained as there are three acoustic, three infrared and three Raman branches at each point.

3. Calculation of the frequencies from L and X.

— The exact expressions for the frequencies of the fourteen degenerate modes in terms of five independent force constants taking into account the influence of the first three neighbours of each atom has been given by Ramanathan [3]. The total number of neighbours taken into account is 20 for each " Ca " and 22 for each " F ". The force constants P_1 and P_2 represent the force on the atom Ca or F due to its own displacement. Q represents the force on " Ca " or " F " due to the displacement of the corresponding nearest neighbours. T_1, T_2 and V take into account the forces on Ca and F due to the displacement of the second and third neighbours respectively. In the language of lattice dynamics, this scheme is a " central force field " taking into account the "Born-Begbie " [9] force constants. The P_1 and P_2 are the self-forces which appear in the Born-Begbie schemes. To calculate these force constants, a knowledge of the activities of these modes in the second-order spectra should be known. In general, the octaves of the vibrations of the octahedral planes of atoms can be expected to appear with considerable intensity in the second-order spectra. Hence, identifying 838 and 408 as $2\nu_9$ and $2\nu_{14}$ and 254 and 322 as ν_1 and ν_2 the infrared active and Raman active fundamentals respectively, the five force constants were calculated. An additional relation

$$(P_1 + 8T_1) = -8Q = 2(P_2 + T_2 + 8V)$$

exists between the force constants and hence it is sufficient to identify the four frequencies. The following are the force constants : (all × 10^4 dynes/cm)

$$\begin{array}{llll} P_1 = & 16.8015 & P_2 = & 13.7873 \\ Q = - & 0.9359 & T_1 = - & 1.1643 \\ T_2 = - & 1.9940 & V = - & 0.7570 \end{array}$$

With these force constants, the frequencies of the other modes were calculated and are shown in Table I along with those obtained from Ganesan and Srinivasan' models I and II.

4. Second-order spectrum.

— The selection rules for two phonon scattering were worked out for the combinations of the phonon branches from the critical point X in the following way. In the Born and Bradburn theory [10] of the Raman spectrum of a cubic crystal due to two-phonon combinations for the same wavevector, a combination

$$\omega\begin{pmatrix} q \\ \overline{jj'} \end{pmatrix} = \omega\begin{pmatrix} q \\ j \end{pmatrix} \pm \omega\begin{pmatrix} q \\ j' \end{pmatrix} \tag{1}$$

between j and j' at $\mathbf{q}$ is permitted, if the contribution to the polarisability by the quadratic terms $\alpha^{(2)}_{\rho\sigma}$ in the Taylor expansion

$$\alpha_{\rho\sigma} = \alpha^{(0)}_{\rho\sigma} + \alpha^{(1)}_{\rho\sigma} + \alpha^{(2)}_{\rho\sigma} \tag{2}$$

does not vanish. These factors $\alpha^{(2)}_{\rho\sigma}$ are given by

$$\alpha_{\rho\sigma}\begin{pmatrix} q \\ jj' \end{pmatrix} = \sum_{l} \sum_{KK'} \sum_{\mu\nu} \alpha_{\rho\sigma,\mu\nu}\begin{pmatrix} l \\ \overline{KK'} \end{pmatrix}$$

$$e^{i\mathbf{q}\cdot\gamma l}\, e_{\mu}\left(K\middle| \begin{matrix} q \\ j \end{matrix}\right) e^{*}_{\nu}\left(K\middle| \begin{matrix} q \\ j' \end{matrix}\right) \frac{1}{\sqrt{m_K m_{K'}}} \cdot$$

and depend on the fourth rank polarisability $\alpha_{\rho\sigma,\mu\upsilon}\begin{pmatrix} l \\ KK' \end{pmatrix}$ tensor components for the various interactions and the eigenvectors of the dynamical matrix. The tensor components are assumed to be different from zero for the first neighbour $Ca_1 — F_2$ and $Ca_1 — F_4$ and second-neighbour $F_2 — F_4$ interactions. Application of the symmetry operations of the lattice and the invariance conditions reduce the number of independent parameters of the tensor to eighteen. If the $\alpha_{\rho\sigma,\mu\upsilon}\begin{pmatrix} l \\ KK' \end{pmatrix}$ are extended to the distant neighbours like $Ca_1 — Ca_1$, etc..., more number of non zero parameters are required to characterise this tensor. These parameters, however, would be expected to be comparatively smaller than for the nearest neighbours. Hence, as a first approximation we have not taken them into account in our present calculations. The normalised eigenvectors of the dynamical matrix at X are

$$\begin{array}{lll} j = 1 & e_1(1|1) = 1 & e_2(1|1) = e_3(1|1) = 0 \\ & & e_\alpha(2|1) = e_\alpha(4|1) = 0, \quad \alpha = 1, 2, 3 \\ j = 2 & e_\alpha(1|2) = 0 & \alpha = 1, 2, 3 \\ & e_1(2|2) = \frac{1}{\sqrt{2}} & e_2(2|2) = e_3(2|2) = 0 \\ & e_1(4|2) = -\frac{1}{\sqrt{2}} & e_2(4|2) = e_3(4|2) = 0 \\ j = 3 & e_\alpha(1|3) = 0 & \alpha = 1, 2, 3 \\ & e_1(2|3) = \frac{1}{\sqrt{2}} & e_2(2|3) = e_3(2|3) = 0 \\ & e_1(4|3) = \frac{1}{\sqrt{2}} & e_2(4|3) = e_3(4|3) = 0. \end{array}$$

The other six branches characterise the two independent directions of polarisation of the transverse waves i.e., the y and z directions. The selection rules worked out with these allow only the following combinations

$\nu_3 \pm \nu_5$, $\nu_3 \pm \nu_6$, $\nu_3 \pm \nu_8$, $\nu_4 \pm \nu_7$ and $\nu_6 \pm \nu_8$.

Therefore, it appears that combinations of acoustic and Raman branches are allowed but the infrared branches can combine only with an infrared branch. The selection rules for the " L " point have not been worked out as the exact eigenvectors for the lattice waves are not known. However, it is assumed that all the combinations are allowed from this critical point. Selection rules derived by Smith [11] in a similar way are found to be in accord with those given by Krishnan [12] using the character table for the supercell of diamond, while it departs from those of Birman [13] in that all the combinations are found to be allowed in his work on diamond, ZnS structures, etc...

TABLE II

SECOND-ORDER RAMAN SPECTRUM OF CALCIUM FLUORIDE

RAMAN SHIFTS IN cm^{-1}	ASSIGNMENTS	CALCULATED VALUE
—	—	—
838	$2\nu_9$	838
787	$\nu_3 + \nu_4$	790
744	$\nu_9 + \nu_{13}$	
	$\nu_4 + \nu_7$	754
714	$\nu_9 + \nu_{11}$	722
		662
670	$2\nu_3$	680
	$\nu_3 + \nu_5$	633
635	$\nu_{12} + \nu_{13}$	
	$\nu_{10} + \nu_{14}$	630
603	$2\nu_{11}$	606
572	$\nu_3 + \nu_8$	576
543	$2\nu_6$	530
	$\nu_7 + \nu_8$	540
467	ν_1 (*LO*)	464
408	$2\nu_{14}$	408
337	—	—
332	ν_2	322
275	—	—
254	ν_1 (*TO*)	254
218	$\nu_{10} - \nu_{14}$	226
	$\nu_9 - \nu_{14}$	217
157	$\nu_4 - \nu_7$	164

5. Russell's Raman effect data. — The frequency shifts of the Raman lines recorded by Russell [2] are entered in Table II. Of these, the lines 322 is the Raman active fundamental mode. The infrared active transverse optical mode with a frequency shift of 254 cm^{-1} though inactive in Raman effect, also appears in the spectrum. The Lyddane-Sachs-Teller splitting of the infrared mode gives rise to a longitudinal optical mode which appears in Raman effect with a frequency shift of 467 cm^{-1}. The observed frequency shift is in accordance with the L-S-T formula. They are marked in Table II. It is interesting to note that the frequency shifts of those three modes ν_1 (*LO*), ν_1 (*TO*) and ν_2 agree with those reported by Cribier and others [14] in inelastic neutron scattering experiments. The assignment of the frequencies of the second order Raman lines based on Ramanathan's model is entered in Table II. Most of the lines are satisfactorily explained. The combination $(\nu_3 + \nu_4)$ at 790 cm^{-1}, though forbidden, appears in Raman spectrum. The origin of the lines at 386, 337 and 275 cm^{-1} is, however, not clear. Similar assignments can be given with the model I of Ganesan and Srinivasan ; but some very intense second order Raman lines remain unexplained with their phonon branches. In order to account for the appearance of these, it may be necessary to take into consideration the other critical points or the higher order supercells in the Raman theory.

In conclusion, it is gratifying to note that as in the case of gallium phosphide, the octaves and combinations of the Raman supercell modes which are allowed in the two phonon scattering processes account for all the prominent features of the observed second-order spectrum of fluorspar (1).

(1) Voir Note, p. 745.

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