

SELECTION RULES FOR SECOND ORDER INFRARED AND RAMAN PROCESSES.  
 II. FLUORITE STRUCTURE AND THE INTERPRETATION  
 OF THE SECOND ORDER INFRARED AND RAMAN SPECTRA OF  $\text{CaF}_2$

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**Résumé.** — On attribue aux phonons un groupe théorique de symétrie et donne les règles correspondantes de sélection pour l'absorption infrarouge à deux phonons dans le fluorure de calcium. Les règles de sélection sont assez favorables pour les processus du second ordre dans les deux cas de l'absorption infrarouge et de la diffusion Raman.

Le spectre Raman du second ordre et le spectre infrarouge sont interprétés en termes de fréquences de paires de phonons aux points critiques de la zone de Brillouin, en combinant les courbes théoriques de dispersion de Ganesan et Srinivasan et les données de diffusion de neutrons de Cribier, Farnoux et Jacrot.

**Abstract.** — Group theoretical symmetry assignments for the phonons and the corresponding selection rules for the two phonon infrared absorption and Raman scattering processes for the calcium fluoride structure are given. The selection rules are reasonably favourable for both second order infrared absorption and second order Raman scattering processes. The second order Raman and infrared spectra are interpreted in terms of phonon pair frequencies at the critical points in the Brillouin zone using a combination of the theoretical dispersion curves of Ganesan and Srinivasan and the neutron scattering data of Cribier, Farnoux and Jacrot.

**1. Introduction.** — The fluorite structure has the same space group as the rocksalt structure ( $O_h^2$ ), but has one more atom in the primitive unit cell. This leads to nine branches in the phonon spectrum with two sets of optical branches, one set having the appropriate symmetry to scatter light in first order and the other set having the appropriate symmetry to absorb light in the first order. Thus  $\text{CaF}_2$  exhibits a first order infrared absorption spectrum [1] and a first order Raman spectrum [2]. Furthermore both the second order infrared absorption spectrum and the second order Raman spectrum of  $\text{CaF}_2$  exhibit appreciable structure. As shown in Section 2, this is due to relatively favourable selection rules for both the infrared and Raman scattering processes [3]. In the present paper we show that the peaks in the second order infrared absorption and Raman spectra of  $\text{CaF}_2$  can be reasonably accounted for by pairs of phonon frequencies at the critical points in the f. c. c. Brillouin zone. The analysis of the structure in the observed spectra was carried out in terms of the selection rules using a combination of the neutron scattering data of Cribier, Farnoux and Jacrot [4] and the theoretical dispersion curves of Ganesan and Srinivasan [5].

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**2. Symmetry of the phonons and the selection rules in calcium fluoride structures.** — The calcium fluoride structure consists of three interpenetrating face-centered cubic lattices each displaced with respect to the other along the body diagonal. The positions of the atoms in the unit cell are : calcium (000) and the two fluorines at  $(1/4, 1/4, 1/4)$  and  $(3/4, 3/4, 3/4)$ . There is a center of inversion between the two fluorines. As the space group is symmorphic, there are no screws or glides. Using group theoretical methods we analyze the symmetries of the various phonons in the Brillouin zone and determine the combination of the phonons which will be active in second order Raman and infrared processes. Only those phonon combinations associated with a high combined density of states per unit wave vector interval participate, and these are generally situated along the symmetry directions and on the zone boundaries.

The lattice dynamics of  $\text{CaF}_2$  was worked out by Ganesan and Srinivasan [5] using a point ion model with an appropriate effective charge on the ions to take into account the polarizability of the ions. Their results have successfully explained the specific heat, thermal expansion and the diffuse X-ray scattering. The dispersion curves obtained experimentally by inelastic neutron scattering by Cribier, Farnoux and Jacrot [4] along the [100] and [111] directions agree very well with the theoretical dispersion curves. These are given along

with the theoretical dispersion curve for the [110] direction in figures 1 and 2. The solid lines are the theoretical curves and the circles are the neutron data. These curves indicate that there are critical points at  $\Lambda$  and  $\Sigma$  points along with those at  $\Gamma$ , X and L. Since dispersion data are not available at other possible critical points, our analysis is based only on these symmetry points.

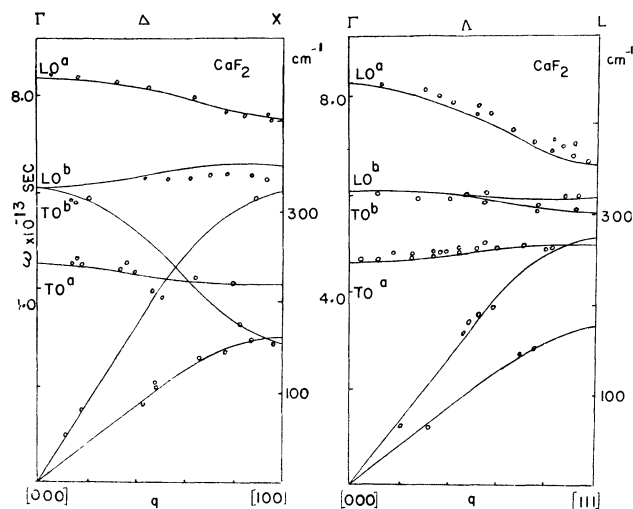


FIG. 1. — Frequency versus wave vector curve along [100] and [111] directions.

Solid line: theory, small circles: neutron data.

(After S. Ganesan and R. Srinivasan [5], D. Cribier, B. Farnoux and B. Jacrot [4].)

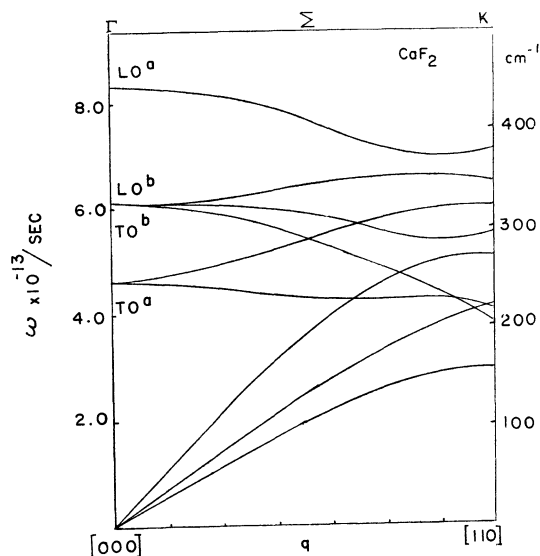


FIG. 2. — Frequency versus wave vector curve along [110] direction. (S. Ganesan and R. Srinivasan [5].)

In a crystal each normal mode transforms according to one of the space group irreducible representations. By placing displacement vectors on the three atoms and using the projection operator

technique, we find out the transformation properties of the various phonons. First we find the phonon symmetries at the center of the Brillouin zone. It turns out that in the optical branches the vibrations fall into two types. In the first type the calcium remains at rest and the two fluorines vibrate against each other. This mode of vibration which is triply degenerate has even parity and hence is Raman active but infrared inactive in first order processes. In the second type, the two fluorines move together and the calcium vibrates against the motion of the fluorines. This is again similar to the diatomic case, where we have two entities moving against each other in the optical branch. This mode of vibration has odd parity and hence is infrared active but Raman inactive in first order processes. Due to the electric field associated with the longitudinal motion of this type, the  $LO$  mode as a higher frequency than the  $TO$  modes. Thus calcium fluoride type crystals exhibit one line in first order Raman scattering and one peak in first order infrared absorption.

For wave vectors along the symmetric directions [100], [111], and [110], the assignment of the phonon symmetries are straightforward and unambiguous as can be seen from the compatibility relations along these directions. When we reach the zone boundaries along these various directions, i.e., at point X, L, etc... we find that each phonon is compatible with two possible symmetry assignments. But the chief feature is that the two assignments possible for each phonon have distinct parity, one is even and the other is odd. Using the fact that in the calcium fluoride structure the motion in the optical branches is similar to the diatomic case, i.e. only two entities are involved, we find that we can assign the phonon symmetries without a knowledge of the actual eigenvectors.

In the infrared motion, we have the calcium moving against the two fluorines, which move in unison. With a center of inversion present between the two fluorines, this type of motion has odd parity. In the Raman motion, we have the calcium at rest and the two fluorines move against each other. As in the case of the diatomic crystals, the amplitude of one decreases as we go to the zone boundary and hence we have again odd parity in this type of motion. This situation is a bit different in the acoustic motion. All the atoms move together at zero wave vector. As we reach the zone boundary, we again find out the motion of the two fluorines. The amplitude of the two fluorines will be the same but the phases may be different. The phase of the motion is given by

$\mathbf{q} \cdot \mathbf{x} \begin{pmatrix} l \\ k \end{pmatrix}$ , where  $\mathbf{q}$  is the vector,  $\mathbf{x}$  is the atomic displacement,  $l$  is the cell index and  $k$  is the the particle index. Since we are dealing with atoms in the same unit cell, this become  $\mathbf{q} \cdot \mathbf{x}(k)$ . For

the X point the phase difference between the two fluorines is  $\pi$  and hence the motion has even parity. For the L point the phase difference between them is  $3/2\pi$  and they have odd parity. This assignment for the L point differs from that given by Loudon [6], who finds even as well as odd parity modes. The symmetry character of the phonons is summarized in Table I.

The electric dipole operator for infrared dipole absorption transforms as  $\Gamma_{15}$  and the polarizability operator for Raman scattering transforms as  $\Gamma_1 + \Gamma_{12} + \Gamma'_{25}$ . We take the phonons in pairs at each wave vector for all the wave vectors considered and work out the selection rules in the usual way by forming the ordinary Kronecker squares and the symmetrized Kronecker squares. We find that for the two phonon Raman scattering, the selection rules allow many combinations of phonons. These are given in Table II. At the center of the zone, the Raman (even) mode does not combine with the infrared (odd) mode and

TABLE I

SYMMETRY POINTS AND PHONON SPECIES IN CALCIUM FLUORIDE STRUCTURE  $O_h^F$

SYMMETRY POINT	PHONON SPECIES
$\bar{\Gamma}$	$\Gamma_{15} (A) + \Gamma_{15} (O^a) + \Gamma'_{25} (O^b)$
$\Delta$	$\Delta_1 (LO^a) + \Delta_5 (TO^a) + \Delta'_2 (LO^b)$ + $\Delta_5 (TO^b) + \Delta_1 (LA) + \Delta_5 (TA)$
X	$X'_4 (LO^a) + X'_5 (TO^a)$ + $X'_2 (LO^b) + X'_5 (TO^b)$ + $X_1 (LA) + X_5 (TA)$
$\Lambda$	$\Lambda_1 (LO^a) + \Lambda_3 (TO^a) + \Lambda_1 (LO^b)$ + $\Lambda_3 (TO^b) + \Lambda_1 (LA) + \Lambda_3 (TA)$
L	$L'_2 (LO^a) + L'_3 (TO^a) + L'_2 (LO^b)$ + $L'_3 (TO^b) + L'_2 (LA) + L'_3 (TA)$
$\Sigma$	$\Sigma_1 (LO^a) + \Sigma_3 (TO^a) + \Sigma_4 (TO^a)$ + $\Sigma_1 (LO^b) + \Sigma_2 (TO^b) + \Sigma_3 (TO^b)$ + $\Sigma_1 (LA) + \Sigma_3 (TA_1) + \Sigma_4 (TA_2)$

TABLE II

TWO PHONON RAMAN ACTIVE PROCESSES IN CALCIUM FLUORIDE STRUCTURES

SYMMETRY POINT	ACTIVITY
$\bar{\Gamma}$ (3)	All combinations except $\Gamma_{15} + \Gamma'_{25}$
X (3)	All combinations except those between acoustic modes (even parity) and optical modes (odd parity)
L (3)	All combinations
$\Delta$	All combinations
$\Lambda$	All combinations
$\Sigma$	All combinations

(3) These exhibit to complementarity in the selection rules between Raman and infrared processes.

TABLE III

TWO PHONON INFRARED PROCESSES IN CALCIUM FLUORIDE STRUCTURES

SYMMETRY POINT	ACTIVITY
—	—
	No overtones in any
$\bar{\Gamma}$ (4)	$\Gamma_{15} + \Gamma'_{25}$
X (4)	$LA + LO^a, LA + TO^a$ $LA + TO^b, TA + LO^a$ $TA + TO^a, TA + LO^b$ $TA + TO^b$
L (4)	None
$\Delta$	All combinations except $LO^b + LO^a$ and $LO^b + LA$
$\Lambda$	All combinations
$\Sigma$	All combinations except $\Sigma_1 + \Sigma_2$ and $\Sigma_3 + \Sigma_4$

(4) These exhibit complementarity in the selection rules between Raman and infrared processes.

at the X point the odd parity modes do not combine with the even parity modes. Thus, at the X point the acoustic modes which have even parity, do not combine with the optical modes which have odd parity. At other points all combinations are allowed. The corresponding selection rules for the two phonon infrared processes are given in Table III. We see that at  $\bar{\Gamma}$ , X and L, they are complementary to the Raman selection rules, i.e., those combinations which are not allowed in Raman scattering at  $\bar{\Gamma}$ , X and L, are allowed in infrared absorption and vice versa.

**3. Interpretation of the second order Raman and infrared spectra of calcium fluoride.** (5) — The second order Raman spectrum of calcium fluoride was recently investigated by Russell [7] using an He-Ne laser and photographic recording. The spectrum which he obtained exhibited 18 peaks of varying intensity in addition to the first order Raman line at  $322 \text{ cm}^{-1}$ . By using the selection rules for the  $\text{CaF}_2$  structure and a combination of the neutron scattering data and theoretical phonon dispersion curves, we were able to arrive at phonon pair assignments for the peaks in the observed spectrum. However, shortly after submitting our manuscript, Gee, O'Shea and Cummins [8] have shown that the structure observed by Russell is due to impurity fluorescence and cannot therefore (6) be attributed to second order Raman scattering.

(5) The discussion of the second order Raman spectrum given in this section has been modified in proof.

(6) One of Professor Cummins' students actually obtained a fluorescence spectrum, using a continuous light source, which exhibited the same structure. Moreover, he was able to identify the peaks as electronic transitions of the  $\text{Er}^{+3}$  ion.

Our phonon pair assignments are accordingly completely invalid. That it was possible to make what appeared to be unambiguous phonon pair assignments based on the experimental and theoretical phonon dispersion curves remains a "minor" puzzle.

The second order infrared absorption spectrum of  $\text{CaF}_2$  was measured by Fray, Johnson and Quarrington [9] (fig. 3). They have interpreted

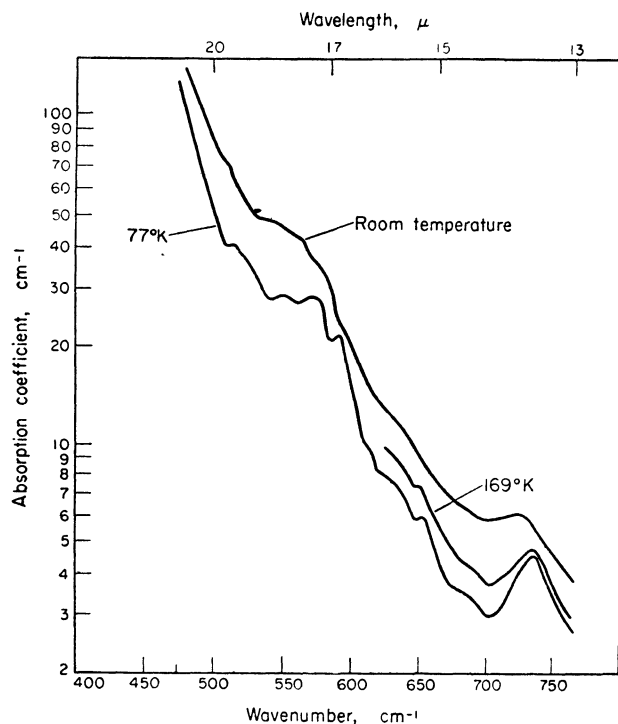


FIG. 3. — Infrared spectrum of calcium fluoride. (S. J. Fray, F. A. Johnson and J. E. Quarrington [9].)

the structure as two phonon combinations and overtone bands involving five characteristic phonon frequencies which they assume to correspond to the phonon branches at the L point. Their assignments are clearly in contradiction to the selection rules for the  $\text{CaF}_2$  structure which rule out all phonon pair combinations at the L point and to the selection rules which forbids overtones when there is a center of symmetry. Applying the selection rules and making use of the theoretical and the experimental neutron dispersion data, we find that the structure in the second order infrared spectrum of  $\text{CaF}_2$  arises primarily from phonon pairs at the  $\Sigma$  point (Table IV).

TABLE IV

SECOND-ORDER INFRARED SPECTRUM IN  $\text{CaF}_2$

EXPERIMENTAL IN $\text{cm}^{-1}$ (JOHNSON ET AL.)	ASSIGNMENT	CALCULATED
735	—	—
690	$LO^a(\Sigma) + TO_1^a(\Sigma)$	685
652	$LO^b(\Sigma) + TO_1^a(\Sigma)$	662
629	$LO^a(\Sigma) + LA(\Sigma)$	634
613	$LA(\Sigma) + LO^b(\Sigma)$	612
590	$LO^a(\Sigma) + TO_2^a(\Sigma)$	592
	$LA(\Sigma) + TO_1^a(\Sigma)$	586
	$TA(X) + LO^a(X)$	583
572	$LO^b(\Sigma) + TO_2^a(\Sigma)$	570
	$LA(X) + TO^a(X)$	574
549	$TO_1^b(\Sigma) + LA(\Sigma)$	551
527	$LO^a(\Sigma) + TA_2(\Sigma)$	523
516	$TO_1^b(\Sigma) + TO_2^a(\Sigma)$	510
475	$TA_2(\Sigma) + TO_1^a(\Sigma)$	475

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