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THE RAMAN SPECTRUM OF GALLIUM PHOSPHIDE

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Résumé. — Les spectres Raman de 1^{er} et 2^e ordre du phosphore de gallium, récemment enregistrés par Russell et Hobden en utilisant un laser He-Ne (¹), sont discutés à partir des théories usuelles de la dynamique des réseaux cristallins. Les spectres observés de GaP sont examinés en détail, avec calcul des fréquences des phonons à partir des points critiques Γ , L et X , en utilisant les modes de super mailles de Raman et l'expression de leurs fréquences donnée par Ramanathan pour le réseau de ZnS. On explique ainsi de façon satisfaisante les fréquences du second ordre observées pour GaP.

Abstract. — The first and second-order Raman spectra of gallium phosphide recorded recently by Russell and Hobden using a He-Ne laser source, are discussed in the light of current theories on the dynamics of crystal lattices. The observed spectra of GaP is examined in detail with a calculation of the phonon frequencies from the critical points Γ , L and X , using the Raman supercell modes and their frequency expressions as given by Ramanathan for ZnS lattice. Satisfactory explanations have been given for the observed second-order frequencies in the case of GaP.

1. Introduction. — Recently, the first and second order Raman spectra of gallium phosphide (GaP) have been recorded for the first time by Hobden and Russell [1] using the intense monochromatic light beam at λ 6328 Å available from a He-Ne laser. The observed Raman spectrum of GaP has been interpreted by these authors with the Γ , L and X critical point phonon energies chosen more or less arbitrarily to fit the Raman shifts. In a recent paper, Krishnan [2] has pointed out that this method of explaining the Raman spectra by considering the presence of singularities in the frequency spectra is exactly similar to the ideas of Raman in postulating supercell modes. Since the critical points L , X , for example, for NaCl structure and R , M and X for CsCl structures, are situated at the extremities of the dispersion curves along [111], [100] or [110] directions, they involve a phase difference of π at least along one of the axes. The transverse and longitudinal phonon branches at these points correspond to the tangential and normal oscillations of these planes of atoms. A further subdivision into optical and acoustical branches is closely related to the physical picture of the supercell modes; their degeneracy being a consequence of the statistical weights of the critical points. Thus the Raman picture postulated in 1943 is an extremely practicable and simple method for explaining the prominent second order processes in light scattering and has now received full justification from the critical point analysis of Birman, Loudon and Johnson. Since gallium phosphide belongs to the zinc blende structure whose vibration spectrum based on the Raman lattice dynamics has already

been worked out by Ramanathan [3] an analysis of the observed second order Raman spectrum is carried out using the nine degenerate modes of the supercell.

2. Theoretical considerations. — 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 observed in these cubic diatomic crystals. The second-order Raman scattering and infrared absorption processes in these crystals are of immense help in giving us an insight to the true nature of the vibration spectra of crystals and have clearly brought out the fact that the Van Hove singularities in the frequency distribution functions are reflected in these two phonon spectra as slope discontinuities in the Raman scattering intensity or in the infrared absorption coefficient. It has been shown by Johnson and Loudon [4] that most of the prominent features of the phonon spectra of diamond, silicon and germanium could be well explained with the Γ , L and X critical point frequencies and that the Raman effect is a valuable source of experimental information on the phonon frequencies at points in the Brillouin zone other than the centre. Second-order Raman scattering in particular can give information complementary to that of infrared absorption, as the critical points which show up as slope discontinuities in the Raman scattering intensity do not contribute in a similar way to the absorption coefficient.

Since the critical points L and X in particular are situated at the extremities of the phonon dispersion curves along the symmetry directions [111]

(¹) Voir communication de Russell au présent Colloque.

and [100], the atomic vibrations correspond to whole planes of atoms moving in phase. For a lattice wave with wavevector \mathbf{k} the phase difference between the identical particles in the adjacent cells is given by $\Phi = 2\pi(\mathbf{k} \cdot \mathbf{r}')$ where \mathbf{r}' is the vector distance between the two particles. Thus for the critical points L and X , these phase differences are 0 or π and the ratio of the amplitudes of identical particles, in adjacent cells (α, β, γ) in the three directions can be $+1$ or -1 . This condition is the starting point of the dynamics of crystals put forward by Raman.

In Raman lattice dynamics, the amplitude ratios of the vibrations of successive equivalent atoms respectively along the three axes of the supercell can be

$$\alpha = \pm 1, \quad \beta = \pm 1 \quad \text{and} \quad \gamma = \pm 1.$$

Thus there are eight possible cases all of which are covered by the following description "Equivalent atoms in the crystal have the same amplitude of vibration, their phases being either the same or else opposite in successive cells of the lattice along each of its three axes". The modes described by $\alpha = 1, \beta = 1$ and $\gamma = 1$, may be pictured as oscillations with respect of each other of the p interpenetrating Bravais lattices of atoms of which the crystal is built up. There would be $(3p - 3)$ such modes, while the other 3 degrees of freedom may be identified as simple translations of the entire crystal. The remaining 21 p normal

modes may be pictured as oscillations relative to each other of the alternate planes of equivalent atoms in the crystal. The case, $\alpha = \beta = 1$ and $\gamma = -1$ corresponds to oscillations of alternate planes of atoms, containing the α and β axes and intersecting the γ axis, against each other. If $\alpha = 1, \beta = \gamma = -1$, the alternate planes of atoms passing through the α axis and cutting both the β and γ axes would oscillate against each other. If $\alpha = \beta = \gamma = -1$, the oscillating planes of atoms would intersect all the three axes at the appropriate angles. In a face-centred cubic structure, these oscillating planes of atoms would be those respectively parallel to the cubic and octahedral planes. These 21 p modes reduce to eight degenerate modes due to presence of three sets of cubic and four sets of octahedral planes in the structure. If we consider a zinc blende lattice, the zinc and sulphur atoms form face-centred cubic lattices, which interpenetrate each other. There are four layers of atoms (alternately Zn and S) parallel to the octahedral and cubic planes. The 48 supercell modes for the structure therefore fall into the two sets — one set representing movements of the adjacent Zn and S atoms in phase, while in the other they are in opposite phases. A description of these modes as given by Ramanathan [3] are entered in Table 1.

3. Calculation of the frequencies at L and X . — The expressions for the frequencies of the nine

TABLE I
VIBRATION SPECTRUM OF GALLIUM PHOSPHIDE

MODE	DEGENERACY	OSCILLATING UNITS	DIRECTION OF OSCILLATION	FREQUENCY IN WAVE NUMBER	$4\pi^2 c^2 m_A \nu^2$
$\nu_1 (T) TO$	3	The two lattices	arbitrary	367 (2)	$\frac{P_1}{m_1} + \frac{P_2}{m_2} = -\frac{4Q}{\mu}$
$\nu_1 (L) LO$	4	(111) planes	normal	329	$\frac{P_1}{m_1} + \frac{P_2}{m_2} - \frac{P_1 P_2 - (2Q - 4R)^2}{P_1 m_2 + P_2 m_1}$
$\nu_2 (L) LA$	4	"	"	162	$\frac{P_1 P_2 - (2Q - 4R)^2}{P_1 m_2 + P_2 m_1}$
$\nu_3 (L) TO$	8	"	tangential	359 (2)	$\frac{P_1}{m_1} + \frac{P_2}{m_2} - \frac{P_1 P_2 - (2Q + 2R)^2}{P_1 m_2 + P_2 m_1}$
$\nu_4 (L) TA$	8]	"	"	76	$\frac{P_1 P_2 - (2Q + 2R)^2}{P_1 m_2 + P_2 m_1}$
$\nu_1 (X) LO$	3	(100) planes	normal	204	$\frac{P_1}{m_1}$
$\nu_2 (X) LA$	3	"	"	305	$\frac{P_2}{m_2}$
$\nu_3 (X) TO$	6	"	tangential	352	$\frac{P_1}{m_1} + \frac{P_2}{m_2} - \frac{P_1 P_2 - 16R^2}{P_1 m_2 + P_2 m_1}$
$\nu_4 (X) TA$	6	"	"	104	$\frac{P_1 P_2 - 16R^2}{P_1 m_2 + P_2 m_1}$

(2) Frequencies which are assumed,

degenerate supercell modes of the ZnS lattice has been worked out by Ramanathan, taking into account the influence of the sixteen atoms surrounding every atom in the crystal. These expressions involve ten force-constants which have to be calculated by identifying some of these modes in the observed spectra. To reduce the number of force constants to be calculated from the observed spectra, we assume only the interaction between an atom and its nearest neighbours. The expressions for $[4\pi^2 c^2 m_h \nu^2]$ given in the 6th column of Table I are therefore more simplified than those given by Ramanathan. P_1 or P_2 is the force on any atom 1 or 2 due to its own displacement along any one of the three cube axes. Q is the force on atom 1 or 2 at the origin due to the displacement of any one of its four nearest neighbours. The direction of both force and displacement is along any one of the three cube axes for the nearest neighbours. R is similarly the force on atom 1 or 2 due to the displacement of its first neighbours, the force and displacement being along two different cubic axes.

In the present case, we have to determine only two force constants Q and R since the other two force constants P_1 and P_2 which appear in the formula in Table I are related by the condition $P_1 = P_2 = -4Q$. In order to calculate the values of Q and R only two frequencies should be identified. It is easy to identify the infrared fundamental, $\nu_1(\Gamma)$ *TO* appearing with a frequency shift of 367 cm^{-1} . The second frequency is the 718 cm^{-1} which is identified as the octave of the vibration of the octahedral planes of atoms with the adjacent Ga and P atoms in opposite phase i.e., $\nu_3(L)$ *TO*. The force constants Q and R were calculated and were found to be

$$Q = -0.4296 \text{ and } R = -0.3379 (10^5 \text{ dynes/cm}).$$

Using these force constants, the frequencies of the other seven modes were calculated and are entered in column 5 of Table I. Of these, only $\nu_1(\Gamma)$ *TO* mode appears as fundamental in the Raman spectrum. The corresponding longitudinal optical mode $\nu_2(\Gamma)$ *LO* also appears in the first order spectrum with a frequency shift of 404 cm^{-1} .

In the second order spectrum of GaP, Hobden and Russell have identified 17 peaks the frequency shifts of which are listed in Table II. Using the selection rules given by Birman [5] for two phonon Raman scattering for the Zn-S structure, fourteen out of the seventeen second order Raman lines are accounted for as the octaves and the allowed combinations of the fundamental modes of GaP lattice. The calculated values of the frequency shifts and the assignments are entered in Table II. The combination $\nu_2(X) + \nu_4(X)$ (409 cm^{-1}) falls adjacent to the fundamental $\nu_2(\Gamma)$ *LO*. The

agreement is quite satisfactory except for the line with the highest wave number shift. If the frequencies for the fundamental modes are calculated after introducing suitable parameters in Ramanathan's expressions to take into account the ionic

TABLE II

SECOND ORDER RAMAN SPECTRUM OF GALLIUM PHOSPHIDE

	OBSERVED FREQUENCY SHIFTS IN cm^{-1}	COMBINATIONAL MODES	CALCULATED FREQUENCY SHIFTS IN cm^{-1}
1	185	$\nu_3(L) - \nu_2(L)$	197
2	210	$2\nu_4(X)$	208
3	255	$\nu_3(X) - \nu_4(X)$	248
4	277	$\nu_3(L) - \nu_4(L)$	283
5	325	$2\nu_2(L)$	324
6	454	$\nu_3(X) + \nu_4(X)$	456
7	464		
8	479	$\nu_1(L) + \nu_2(L)$	491
9	529	$\nu_2(L) + \nu_3(L)$	521
10	555	$\nu_2(X) + \nu_3(X)$	556 $\frac{1}{2}$
11	579		
12	603	$2\nu_2(X)$	610
13	684	$\nu_1(L) + \nu_3(L)$	688
14	718	$2\nu_3(L)$	718
15	736	$2\nu_1(\Gamma)$ <i>TO</i>	734
16	752		
17	782	$2\nu_2(\Gamma)$ <i>LO</i>	808

and piezoelectric effects, the agreement between the observed and calculated shifts of the fourteen second order Raman lines will be better.

It is thus seen that the octaves and combinations of the supercell modes which are allowed in the two phonon scattering processes account for most of the prominent features of the observed second order spectrum of GaP. In order to account for the appearance of the three remaining Raman lines, it is necessary to take into consideration the other critical points like *W* and *K* or the higher order supercells in the Raman theory.

To conclude, it is of interest to note that the Raman dynamics correctly predicts the accidental degeneracy of the longitudinal optical and longitudinal acoustic modes at the zone boundary *X* (100) for the diamond structure and also gives a sum rule for the lattice vibration frequencies as can be seen from the dynamical models of Ramanathan. With suitable modifications of the theoretical expressions taking into account the ionic

and piezoelectric effects, the Raman dynamics offers a physical and quantitative account of the supercell modes of not only the cubic lattices but all the 14 Bravais lattices and the hexagonal close packed structure [6]. The octaves and combinations of the supercell modes which are allowed in the two phonon scattering processes account for most of the prominent features of the observed second order Raman spectrum. If one wants to introduce the other critical points like those along Σ , Δ , Λ , detailed theory can be worked out taking into account higher order supercells.

Discussion

M. THEIMER. — Is the number of “ Raman-modes ” always equal to the number of observed peaks in the 2.-order spectrum, or is it in general larger or smaller ?

M. BIRMAN. — Does your force constant model calculation enable you to check the $\omega(\mathbf{K})$ calculated, with experimental results ? In particular, did you calculate elastic constants in CaF_2 and compare with experiments ? How good was the agreement ?

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