

## Spectral intensities of two-phonon transitions in stressed zinc-blende lattices

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(Received 29 August 1973)

The Raman and infrared transition intensities are calculated for the two-phonon processes in stressed zinc-blende- and diamond-type crystals. The number of split levels of two-phonon states and the remaining degeneracies for highly symmetric modes and strain configurations can be evaluated by simple inspection. The relative intensities of these sublevels are calculated for the three Raman components  $\Gamma_1$ ,  $\Gamma_2$ , and  $\Gamma_{15}$  and for the infrared absorption ( $\Gamma_{15}$ ). The  $\Gamma_1$  component is found to be less suitable in studies where the broadening of the spectra are larger than the attainable splitting, while the optical anisotropy induced in the  $\Gamma_{12}$  and  $\Gamma_{15}$  components may be informative for a number of two-phonon transitions.

### I. INTRODUCTION

Second-order infrared and Raman spectra of lattice vibrations have been subject to extensive investigations<sup>1,2</sup> since these provide information on vibrational frequencies at several points in the first Brillouin zone. In crystals with high symmetries, however, the identification of the observed singularities is difficult due to the pronounced degeneracy of the two-phonon states involved and the high degree of optical symmetry of the crystals. So far, informative perturbations on two-phonon spectra have been hydrostatic pressure,<sup>3</sup> resonance-Raman experiments,<sup>4</sup> and alloying,<sup>5</sup> while perturbations reducing the symmetry have not been reported. Thus various theoretical models and inelastic neutron scattering have been the principal sources of information in the assignment of two-phonon spectra.

Uniaxial stress is believed to provide measurable perturbations on these spectra, and so it is important to derive relative intensities for two-phonon transitions in anisotropically stressed crystals. A forthcoming paper<sup>6</sup> will present a discussion of magnitude of the expected splitting of phonon frequencies in diamond- and zinc-blende-type materials, while we here evaluate infrared and Raman selection rules for two-phonon processes, i. e., the intensities of strain-split sublevels as they appear in the three Raman components ( $\Gamma_1$ ,  $\Gamma_{12}$ , and  $\Gamma_{15}$ ) in zinc-blende lattices. The results for the  $\Gamma_{15}$  component can be applied directly to the infrared spectra.

### II. PROCEDURE IN CALCULATION

In our calculation we have not used conventional group theory since a somewhat faster method is obtained by restricting the studies to phonon modes in which both atoms in the unit cell vibrate in the same crystallographic direction (in phase or in opposite phase). We shall return to this restriction later.

The qualitative features of the stress-induced degeneracy removal will be discussed elsewhere.<sup>6</sup> Here we only note that phonons at  $L$  and  $X$  in the presence of [001] and [111] uniaxial stress split according to their polarization and propagation direction with respect to the stress axis. Thus a simple inspection is sufficient for a determination of the number of strain-split sublevels and remaining degeneracy.

Let us consider a phonon with wave vector  $\vec{k}$  at  $X$  or  $L$  in the first Brillouin zone. The mode can be characterized by atomic displacements in the unit cell at  $\vec{R}$  given by

$$\vec{\xi}^{(i)}(\vec{R}) = \vec{\xi}^{(i)} c^i(\vec{k} \cdot \vec{R} - \omega t),$$

where  $i$  denotes the  $i$ th atom in the unit cell, and  $\omega$  is the angular frequency. As mentioned previously we shall here restrict the further considerations to modes where

$$\vec{\xi}^{(i)} = \xi^{(i)} \vec{p},$$

TABLE I. Vibrational directions for the strain-split one-phonon states considered.  $L$  and  $T$  denote longitudinal and transverse modes, respectively, while ( $X$ ) and ( $L$ ) indicate points in the first Brillouin zone of the strain-free crystal. Subscripts  $\alpha$  and  $\beta$  correspond to propagation parallel and nonparallel to the stress axis, respectively. Subscripts 1 and 2 stand for vibration parallel and perpendicular to the plane containing the stress axis and the wave vector.

Mode	STRESS    [001]		STRESS    [111]	
	Sublevel	Vibrational direction	Sublevel	Vibrational direction
$L(X)$	$L_\alpha$	[001]	$L$	[001] and 2 equivalent
	$L_\beta$	[010], [100]		
	$T_\alpha$	[110], [110]		$T_1$
$T(X)$	$T_\beta$	[101], [101], [011], [011]	$T_2$	[110] and 2 eq.
	$L(L)$	$L$	$L_\alpha$	[111]
			[111] and 3 equivalent	$L_\beta$
$T(L)$	$T_1$	[112] and 3 eq.	$T_\alpha$	[110], [112]
	$T_2$	[110] and 3 eq.	$T_{\beta 1}$	[112] and 2 eq.
				$T_{\beta 2}$

TABLE II. Relative Raman intensities of two-phonon spectra for [001] stress. The symbols used for the one-phonon states involved are explained in Table I. Primes and double primes are used to indicate participation of two transverse or two longitudinal phonons. Thus, the last pair of two-phonon states are degenerate for overtones. The superscripts on  $\Gamma_{12}$  and  $\Gamma_{15}$  indicate dependence on polarization configuration. With the cubic axes as basis the corresponding polarization configuration are given in the second line of the table. For a  $x'y'z$  coordinate system rotated  $45^\circ$  about the stress axis, the  $\Gamma_{12}^{(1)}$  and  $\Gamma_{15}^{(1)}$  selection rules appear in the  $x'y'$  and  $x'z'$  (or  $y'y'$ ) polarization, respectively. For infrared absorption the relative intensities for parallel and perpendicular polarization are given by the  $\Gamma_{15}^{(1)}$  and  $\Gamma_{15}^{(2)}$  columns, respectively.

Mode	Split level	$\Gamma_1$	$\Gamma_{12}^{(1)}$ $xx$	$\Gamma_{12}^{(2)}$ $zz$	$\Gamma_{15}^{(1)}$ $xy$	$\Gamma_{15}^{(2)}$ $xz$
$L'(X) \pm L''(X)$	$L'_\alpha \pm L''_\alpha$	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{2}{3}$	...	...
	$L'_\beta \pm L''_\beta$	$\frac{2}{3}$	$\frac{5}{6}$	$\frac{1}{3}$	...	...
$L(X) \pm T(X)$	$L_\alpha \pm T_\alpha$	...	...	...	0	$\frac{1}{2}$
	$L_\beta \pm T_\beta$	...	...	...	1	$\frac{1}{2}$
$T(X) \pm T''(X)$	$T'_\alpha \pm T''_\alpha$	$\frac{1}{3}$	$\frac{5}{12}$	$\frac{1}{6}$	1	0
	$T'_\beta \pm T''_\beta$	$\frac{2}{3}$	$\frac{7}{12}$	$\frac{5}{6}$	0	1
	$L \pm T_1$	...	$\frac{1}{4}$	1	1	$\frac{1}{4}$
$L(L) \pm T(L)$	$L \pm T_2$	...	$\frac{3}{4}$	0	0	$\frac{3}{4}$
	$T'_1 \pm T''_1$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{10}$	$\frac{4}{10}$
	$T'_2 \pm T''_2$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{9}{10}$	0
	$T'_1 \pm T'_2$	0	$\frac{3}{8}$	0	0	$\frac{3}{10}$
	$T'_2 \pm T''_1$	0	$\frac{3}{8}$	0	0	$\frac{3}{10}$

i. e., both atoms in the unit cell vibrate along a common direction given by the unit polarization vector  $\vec{p}$ .

The simultaneous presence of two such modes involves a perturbation proportional to

$$\xi_1 \xi_2 \{\vec{p}_1 \vec{p}_2\} \times \exp\{i[(\vec{k}_1 \pm \vec{k}_2) \cdot \vec{R} + (\omega_1 \pm \omega_2)t]\},$$

where  $\xi_1$  and  $\xi_2$  denote scalar amplitudes for phonon 1 and 2, respectively, and  $\{\vec{p}_1 \vec{p}_2\}$  is the dyadic product of the two polarization vectors involved. In case of changes in the ( $\vec{k} \approx 0$ ) polarizability tensor  $\alpha$ , a general form would be

$$\Delta \alpha_{ij} = \xi_1 \xi_2 \sum_{kl} q_{ijkl} (p_{1k} p_{2l}) \times e^{-i(\omega_1 \pm \omega_2)t}.$$

Considering only symmetric Raman tensors we

replace  $p_{1k} p_{2l}$  with the symmetrized form

$$\pi_{kl} = \frac{1}{2} (p_{1k} p_{2l} + p_{1l} p_{2k}),$$

where we have dropped the index specifying the pair of phonons with  $\vec{k}_1 \pm \vec{k}_2 = 0$ . The fourth-rank tensor  $q_{ijkl}$  thus connects two symmetric second-rank tensors and such tensors in cubic lattices have only three different elements:  $q_{11}$ ,  $q_{1122}$ , and  $q_{1212}$  if we use the cubic axes as basis.<sup>7</sup> Then we may write

$$\Delta \alpha = \frac{1}{3} a \begin{pmatrix} \pi_0 & 0 & 0 \\ 0 & \pi_0 & 0 \\ 0 & 0 & \pi_0 \end{pmatrix} + \frac{1}{3} b \times \left\{ \begin{pmatrix} 3\pi_{11} - \pi_0 & 0 & 0 \\ 0 & 3\pi_{22} - \pi_0 & 0 \\ 0 & 0 & 3\pi_{33} - \pi_0 \end{pmatrix} + d \begin{pmatrix} 0 & \pi_{12} & \pi_{13} \\ \pi_{12} & 0 & \pi_{23} \\ \pi_{13} & \pi_{21} & 0 \end{pmatrix} \right\},$$

where  $\pi_0$  is the trace of the  $\pi$  tensor and  $a$ ,  $b$ , and  $d$  are coupling coefficients corresponding to the  $\Gamma_1$ ,  $\Gamma_{12}$ , and  $\Gamma_{15}$  components, respectively.

When deriving Raman intensity matrices the above tensor  $\Delta \alpha$  should be transformed into an appropriate coordinate system (unless the intensity matrix is desired for light polarizations along the cubic axes). Let the transformed tensor for

TABLE III. Relative intensities of two-phonon spectra for [111] stress. The symbols used for indication of modes are equivalent to those of Tables I and II. For transverse overtone states the two last pairs of the  $T' \pm T''$  sublevels are degenerate. The polarization configuration (second line) refer to any coordinate system  $x''y''z''$  with  $z'' \parallel$  stress. For infrared absorption the intensities for parallel and perpendicular polarization are given by the  $\Gamma_{15}^{(2)}$  and  $\Gamma_{15}^{(3)}$  columns, respectively.

Mode	Split level	$\Gamma_1$	$\Gamma_{12}$	$\Gamma_{15}^{(1)}$ $x''x''$	$\Gamma_{15}^{(2)}$ $z''z''$	$\Gamma_{15}^{(3)}$ $x''y''$
$L'(L) \pm L''(L)$	$L'_\alpha \pm L''_\alpha$	$\frac{1}{4}$	...	$\frac{1}{4}$	$\frac{3}{4}$	0
	$L'_\beta \pm L''_\beta$	$\frac{3}{4}$	...	$\frac{3}{4}$	$\frac{1}{4}$	1
	$L_\alpha \pm T_\alpha$	...	$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{6}{16}$
$L(L) \pm T(L)$	$L_\beta \pm T_{\beta_1}$	...	$\frac{3}{8}$	$\frac{3}{8}$	1	$\frac{1}{16}$
	$L_\beta \pm T_{\beta_2}$	...	$\frac{3}{8}$	$\frac{3}{8}$	0	$\frac{9}{16}$
	$T'_\alpha \pm T''_\alpha$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{10}{40}$	$\frac{6}{40}$	$\frac{12}{40}$
$T'(L) \pm T''(L)$	$T'_{\beta_1} \pm T''_{\beta_1}$	$\frac{3}{8}$	$\frac{3}{16}$	$\frac{9}{40}$	$\frac{25}{40}$	$\frac{1}{40}$
	$T'_{\beta_2} \pm T''_{\beta_2}$	$\frac{3}{8}$	$\frac{3}{16}$	$\frac{9}{40}$	$\frac{3}{40}$	$\frac{9}{40}$
	$T'_{\beta_1} \pm T'_{\beta_2}$	0	$\frac{3}{16}$	$\frac{6}{40}$	0	$\frac{9}{40}$
	$T'_{\beta_2} \pm T'_{\beta_1}$	0	$\frac{3}{16}$	$\frac{6}{40}$	0	$\frac{9}{40}$
	$L \pm T_1$	...	...	$\frac{1}{2}$	1	$\frac{1}{4}$
$L(X) \pm T(X)$	$L \pm T_2$	...	...	$\frac{1}{2}$	0	$\frac{3}{4}$
	$T'_1 \pm T''_1$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$T'(X) \pm T''(X)$	$T'_2 \pm T''_2$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	$T'_1 \pm T'_2$	0	$\frac{3}{8}$	0	0	0
	$T'_2 \pm T''_1$	0	$\frac{3}{8}$	0	0	0

the  $\nu$ th phonon pair be denoted as  $\Delta \alpha'_\nu$ . Then the intensity matrix of the  $n$ th sublevel of the strain-split two-phonon state is given by

$$R_{ij}^n = \sum [(\Delta \alpha'_\nu)_{ij}]^2,$$

where the summation runs over still degenerate two-phonon states.

In Table I, we list the vibrational directions for eigenmodes in [001]- and [111]-stressed lattices. Also indicated are the groups of modes that are still degenerate in the stressed lattice. Using these findings, we have derived the Raman intensity matrices  $R_{ij}^n$  and examined the relative intensities associated with the three components for  $\Gamma_1$ ,  $\Gamma_{12}$ , and  $\Gamma_{15}$  (coefficients to  $a^2$ ,  $b^2$ , and  $d^2$ , respectively). In Tables II and III, we list these relative intensities as fractions of the intensity at zero stress. For [001] stress we refer to the cubic axes while for [111] stress the matrices are derived for axes given by [111],  $[1\bar{1}0]$ , and  $[11\bar{2}]$ .

Obviously the  $\Gamma_1$  component has common relative intensities for all (diagonal) Raman matrix elements. Similarly, the  $\Gamma_{12}$  component for [111] stress appears to have same relative intensities for all nonzero matrix elements. In the remaining cases there are two or three sets of fractional intensities depending on the polarization configuration.

Note that in Tables I and II, we have neglected the polarization splitting of transverse phonons at  $X$  for [001] stress. Here the modes with  $\vec{k}$  perpendicular to the stress may split into two sublevels, and the corresponding uncoupled eigenmodes are characterized by mutual perpendicular motion (along the cubic axes) of the two atoms in the unit cell. Thus the splitting vanishes in diamond-type lattices while in zinc-blende lattices estimates<sup>6</sup> have established that the splitting is

small even for a mass ratio as that in GaP. In this case we can insert vibrational directions at  $45^\circ$  to the [001] stress axis for transverse phonons with  $\vec{k}$  perpendicular to the stress. Such modes have common vibrational directions for the two atoms in the unit cell and can thus be treated in the above theory. An exact treatment leads to Raman-intensity ratios depending on the mass ratio.

The results for the  $\Gamma_{15}$  component can be applied directly to infrared spectra. The contribution of the sublevels to this absorption when using polarized light are given in Tables II and III as indicated in the table captions.

### III. CONCLUDING REMARKS

The present results can be used in connection with experimental studies of singularities in two-phonon spectra of stressed zinc-blende and diamond lattices. Since the broadening of these singularities (or the resolution) is expected to be larger than the splittings<sup>6</sup> it is essential to know the intensities of two-phonon transitions when measured with different polarization and stress configurations. It is important to note that the  $\Gamma_1$  component is not suitable for such studies. The two-phonon transitions contributing to this component have relative intensities proportional to the remaining degeneracy in the stressed lattice. This implies that the over-all shift of a spectral structure depends only on the volume change. On the other hand the  $\Gamma_{12}$  and  $\Gamma_{15}$  components may be informative even if the splitting is not resolved since the shifts of spectral structures depend in general on the stress and polarization configuration.

### ACKNOWLEDGMENT

The author has benefited greatly from discussions with Professor Cardona.

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