Solid State Communications, Vol. 9, pp. 819–822, 1971. Pergamon Press. Printed in Great Britain

RAMAN TENSOR OF GERMANIUM AND ZINCBLENDE-TYPE SEMICONDUCTORS

M. Cardona

Brown University, Physics Department, Providence, Rhode Island

(*Received* 25 *February* 1971 *by E. Burstein*)

It is shown that the one-phonon Raman tensor of germanium and zincblende-type materials can be calculated from a model density of states consisting only of the E_0 and the $E_0 + \Delta_0$ parabolic critical points. The calculated Raman tensors and their spectral dependence are compared with experimental results for GaP, GaAs, and ZnSe and with a recent calculation for Ge based on the complete band structure.

IT HAS been recently shown that a number of dielectric properties of the germanium and zincblende-type semiconductors can be interpreted on the basis of a very simple model density of states.[1] Among these properties are the piezo-optical constants[2,3] and the first[4] and second order[5] electro-optic effects. The purpose of this letter is to show that the one-phonon Raman tensor and its dispersion can also be obtained from such simple model density of states.

The model density of states mentioned above consists of a parabolic critical point at the energy of the lowest direct gap E_0 with its spin-orbit mate $E_0 + \Delta_0$, a pair of two-dimensional minima E_1 and $E_1 + \Delta_1$, and a strong one-dimensional critical point at the so-called isotropic Penn gap E_2.[6] The Raman scattering cross section due to optical phonons is proportional to the square of the quantity:[7]

$$P = \lim_{\delta \to 0} \frac{a_0^2}{\delta} \chi_{xy}(\omega, \delta), \tag{1}$$

where δ is related to the relative displacement of the two sublattices $a_0/4\,[1 + \delta, 1 + \delta, 1 + \delta]$, produced by the optical phonon, a_0 is the lattice constant and $\chi_{xy}(\omega, \delta)$ is the electric susceptibility tensor for the solid with the sublattice displacement corresponding to δ. The sublattice displacement produced by the optical phonon has the same symmetry ($\Gamma_{25'}$ in Ge, Γ_{15} in zincblende) as a pure shear along [111]. Hence the contributions to P of the E_0, $E_0 + \Delta_0$, E_1 and $E_1 + \Delta_1$ components of our model density of states are formally the same as those found for the elasto-tensor[2,3] with the deformation potentials d, d_1, and $\mathcal{E}_2$ replaced by the appropriate splittings of the corresponding bands produced by the sublattice displacement. We thus find for the contribution to P, of the E_0, $E_0 + \Delta_0$ edges[2] for frequencies below E_0:

$$P(E_0, E_0 + \Delta_0) = \frac{C_0'' a_0^2}{32\pi\,\omega_0}\{-g(x_0) + (4\omega_0/\Delta_0)\,[f(x_0) - (\omega_0/\omega_{0s})^{3/2} f(x_{0s})]\}\,\frac{\delta\omega_0}{\delta}, \tag{2}$$

with:

$$g(x) = (1/x^2)\,[2 - (1 + x)^{-1/2} - (1 - x)^{-1/2}]$$
$$f(x) = (1/x^2)\,[2 - (1 + x)^{1/2} - (1 - x)^{1/2}] \tag{3}$$
$$x_0 = \frac{\omega}{\omega_0}, \quad x_{0s} = \frac{\omega}{\omega_0 + \Delta_0}$$

ω_0 and $\omega_0 + \Delta_0$ are the frequencies of the E_0 and $E_0 + \Delta_0$ gap, respectively. The parameter C_0'' has been defined in reference 2. It can be either calculated from ω_0 and the effective mass of the

$\mathbf{k} = 0$ conduction band or obtained from a fit of the dispersion in the real part of the dielectric constant below E_0. The energy $\delta\omega_0$ is the splitting of the top valence bands produced by the sublattice displacement given by δ. The 'deformation potential' $\delta\omega/\delta$ can be easily obtained from calculations in the literature[8,9] of the deformation potential d for several values of the internal strain parameter ζ. From reference 9 we find $\delta\omega/\delta = 12.3\,\text{eV}$ for germanium.

A similar expression is obtained for the contribution of the E_1 and $E_1 + \Delta_1$ edges. According to references 8 and 9, however, the corresponding deformation potentials are very small [$\sim 1\,\text{eV}$] and hence this contribution is totally negligible below E_0. It should, however, become appreciable near resonance ($\omega \approx \omega_1$ or $\omega \approx \omega_1 + \Delta_1$) and it can be used to fit the resonance observed near E_1 for InAs[10] and near $E_1 + \Delta_1$ for InSb.[11]

The contribution of the nearly isotropic Penn gap[6] is more difficult to estimate because of the uncertainty in the location in $\mathbf{k}$ space of the states contributing to this gap: these states occur at rather general low-symmetry points of $\mathbf{k}$ space. It was shown in reference 3 that the correction and order of magnitude of the contribution of E_2 to the piezo-optical tensor is obtained by assuming that it is produced by the deformation of the isotropic Brillouin zone associated with the stress. For instance, a uniaxial compression produces an extension of the Brillouin zone along its direction and thus an increase in the corresponding energy gap for transitions polarized parallel to the stress direction. On the basis of this argument we conjecture that a sublattice displacement produces no E_2 contribution to the Raman tensor since it does not change the Brillouin zone. This conjecture means, on the basis of the above discussion, that only the E_0, $E_0 + \Delta_0$ contribution is responsible for the Raman tensor and its dispersion below E_0, a result which can be easily tested by comparison with experiments. We show in Fig. 1 the scattering cross section of GaP below E_0, as measured by Scott *et al.*[12] at room temperature. This cross section, in arbitrary units, has been corrected for absorption and for the ω^4 factor and thus is proportional to P^2. The solid line in this figure was calculated with equation 2 with C_0'' adjusted so as to fit the point at 2.7 eV, $E_0 = 2.88\,\text{eV}$ and $\Delta_0 = 0.082\,\text{eV}$[13,14]. We feel that the agreement between the calculated and the measured dispersion of the scattering cross section is very satisfactory, thus confirming the smallness of the E_2 contribution conjectured earlier.

We have also tried to explain in the same manner the dispersion in the scattering cross section observed for ZnSe:[15] We can only account for one-half of the dispersion measured between 2.38 and 2.53 eV. This can be attributed to the fact that exciton effects, not considered in equation (2) are rather strong in ZnSe.

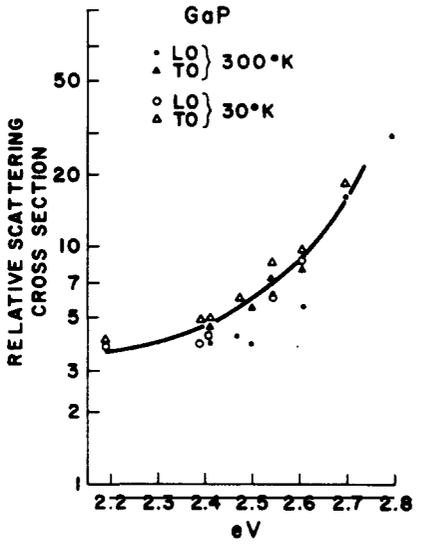

FIG. 1. Dispersion in the Raman scattering cross section (after correction for absorption and for ω^4 law) measured by Scott *et al.*[12] The solid curve is the fit obtained with equation (2).

In order to check the numerical value of the Raman tensor predicted by equation (2) we have compared it with calculations for germanium, based on the complete pseudopotential band structure of this material, performed by Swanson and Maradudin.[7] These calculations were limited to the first four terms in the power series expansion of P as a function of ω^2:

$$P = P^{(0)} + P^{(1)}\,\omega^2 + P^{(2)}\,\omega^4 + P^3\,\omega^6 + \ldots \quad (4)$$

By expanding equation (2) in power series of ω^2 we find:

$$
\begin{aligned}
P^{(0)} &= \beta\{0.75 + \gamma^{-1}[1 - (1+\gamma)^{-3/2}]\} \\
P^{(1)} &= \beta\omega_0^{-2}\{0.548 + 0.313\gamma^{-1}[1 - (1+\gamma)^{-7/2}]\} \\
P^{(2)} &= \beta\omega_0^{-4}\{0.451 + 0.16\gamma^{-1}[1 - (1+\gamma)^{-11/2}]\} \\
P^{(3)} &= \beta\omega_0^{-6}\{0.392 + 0.105\gamma^{-1}[1 - (1+\gamma)^{-15/2}]\}
\end{aligned}
\tag{5}
$$

where β and γ are given by

$$
\beta = \frac{C_0'' \, \delta\omega_0 \, a_0^2}{32\pi \, \omega_0 \, \delta}
\qquad
\gamma = \frac{\Delta_0}{\omega_0}
\tag{6}
$$

The values of $P_0^{(i)}$ calculated for germanium with equation (5) are listed in Table 1. We have taken $C_0'' = 2.57$, the experimental value given in reference 2, $\delta\omega_0/\omega_0 = 12.3\,\text{eV}$,[9] $\Delta_0 = 0.29\,\text{eV}$, $\omega_0 = 0.8\,\text{eV}$ (at room temperature) and $a_0 = 5.62\,\text{Å}$. The values of $P_0^{(i)}$ calculated by Swanson and Maradudin[7] for germanium are also listed in Table 1. Reasonable agreement is obtained for $P^{(0)}$ and $P^{(1)}$ but not for $P^{(2)}$ and especially for $P^{(3)}$. The reason for the disagreement is the fact that the spin-orbit interaction was neglected in reference 7: the large values of $P^{(2)}$ and $P^{(3)}$ are due in part to spin-orbit interaction at the E_0 gap. The sublattice displacement produces a large transfer of oscillator strength between the E_0 and the $E_0 + \Delta_0$ gap which is absent in reference 7. Also, the value of ω_0 in the bands of reference 7 is 1.2 eV [16] instead of 0.8 eV; this fact also contributes (see equation 5) to the small values of $P^{(2)}$ and $P^{(3)}$ found in reference 7.

Johnston and Kaminow [17] have measured the absolute value of the scattering cross section for GaAs at 1.06μ. From their results we obtain $P \simeq 70\,\text{Å}$. Taking $\delta\omega_0/\delta = 12.3$, the same value as for germanium,[18] we find from equation (2) with the known parameters of GaAs ($\lambda = 1.06\mu$) $= 68\,\text{Å}^2$, in excellent agreement with experiment.

Table 1. Calculated coefficients of the expansion of the Raman tensor in power series of ω^2 (see equation 4

	$P^{(0)}$ (Å^2)	$P^{(1)}$ (Å^2 – eV^{-2})	$P^{(2)}$ (Å^2 – eV^{-4})	$P^{(3)}$ (Å^2 – eV^{-6})
Our calculation	22	21	24	31
Reference 7	40.5	17.5	5.4	1.6

REFERENCES

1. CARDONA M., *J. Res. N.B.S.*, **74A**, 253 (1970).
2. HIGGINBOTHAM C.W., CARDONA M. and POLLAK F.H., *Phys. Rev.* **184**, 821 (1969).
3. YU P.Y., POLLAK F.H. and CARDONA M., *Phys. Rev.*, (in press).
4. BELL M., *Proc. Symp. on Electronic Density of States*, Gaithersburg, Md. 1969 (to be published).
5. VAN VECHTEN J.A., CARDONA M., ASPNES D.E. and MARTIN R.M., *Proc. Int. conf. on the Physics of Semiconductors*, Cambridge, Mass., 1970 (U.S. Atomic Energy Commision, 1970). p. 82.
6. PENN D., *Phys. Rev.* **128**, 2093 (1962).
7. SWANSON L.R. and MARADUDIN A.A., *Solid State Commun.* **8**, 859 (1970).
8. GOROFF I. and KLEINMAN L., *Phys. Rev.* **132**, 1080 (1963).
9. MELZ P., Technical Report No. HP–25, Division of Engineering and Applied Physics, Harvardy University.
10. LEITE R.C.C. and SCOTT J.F., *Phys. Rev. Lett.* **21**, 130 (1969).
11. PINCZUK A. and BURSTEIN E., *Phys. Rev. Lett.* **21**, 1073 (1968).

12. SCOTT J.F., DAMEN T.C., LEITE R.C.C. and SILFVAST W.T., *Solid State Commun.* **7**, 953 (1969).
13. DEAN P.J., KAMINSKY G. and ZETTERSTROM R.B., *J. appl. Phys.* **38**, 3551 (1967).
14. SELL D.D. and LAWAETZ P., *Phys. Rev. Lett.* **26**, 311 (1971).
15. LEITE R.C.C., DAMEN T.C. and SCOTT J.F., *Light Scattering in Solids*, p. 359 (edited by WRIGHT G.B.) Springer Verlag, N.Y., (1969).
16. COHEN M.L. and BERGTRESSER T.K., *Phys. Rev.* **141**, 789 (1966).
17. JOHNSTON W.D. and KAMINOW I.P., *Phys. Rev.* **188**, 1209 (1969).
18. LAWAETZ P., to be published.

Der Raman-Tensor des Germaniums und der Materialien mit Zinkblendestruktur wird aus der Modellzustandsdichte berechnet. Diese Modellzustandsdichte besteht nur aus den E_0 und $E_0 + \Delta_0$ parabolischen kritischen Punkten. Die berechneten Raman-Tensoren, und ihre spektrale Abhängigkeit, werden nuit experimentellen Ergebinssen für GaP, GaAs, und ZnSe verglichen. Der Raman-Tensor berechnet Germanium wird mit Rechnungen aus der vollständigen Baudstruktur verglichen.