dynamics cell has made it possible, for the first time, to model a realistic transition from the plastic to the crystalline phase. Many other systems are within the power of the DAP, and it should soon be possible to perform a comprehensive unifying analysis of the wide variety of experimental data available for many of these systems. Furthermore such simulations should stimulate experimental work—the present result clearly indicates the point in the Brillouin zone of the cubic phase which should show evidence of the transition through x-ray diffuse scattering —that is, if the simulation has developed the true natural structure.

[1] J. Timmermans, J. Phys. Chem. Solids 18, 1 (1961).
[2] D. G. Bounds, M. L. Klein, and G. N. Patey, J. Chem. Phys. 72, 5348 (1980).
[3] G. S. Pawley, Mol. Phys. 43, 1321 (1981).
[4] D. Beeman, J. Comput. Phys. 20, 130 (1976).
[5] D. J. Evans, Mol. Phys. 34, 317 (1977).
[6] H. Gostick, I.C.L. Tech. J. 1, 116 (1979).
[7] G. S. Pawley and G. W. Thomas, to be published.
[8] M. Parrinello and A. Rahman, Phys. Rev. Lett. 45, 1196 (1980).
[9] P. R. Salvi and V. Schettino, Chem. Phys. 40, 413–424 (1979).
[10] G. S. Pawley, in *Neutron Inelastic Scattering, 1972* (International Atomic Energy Agency, Vienna, 1972), p. 175–194; R. J. Nelmes and G. S. Pawley, Mol. Cryst. Liq. Cryst. 19, 223 (1973).

Calculation of the Γ-Δ Electron-Phonon and Hole-Phonon Scattering Matrix Elements in Silicon

Orest J. Glembocki and Fred H. Pollak
Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210

(Received 25 November 1981)

With use of the "rigid-pseudoion" model, the first calculation of the electron-phonon and hole-phonon scattering matrix elements for the TO, LO, TA, and LA phonon-assisted indirect transitions (Γ-Δ) in Si has been performed. Excellent agreement with experimental values for the TO phonon is found. Based on the present results, the intensities of the entire Γ-Δ indirect spectrum of this material can be accurately described, thereby rigorously testing the model.

PACS numbers: 63.20.Kr, 72.20.Dp, 78.20.Bh

Although intervalley electron-phonon (e-ph) and hole-phonon (h-ph) interactions play a crucial role in many of the optical[1] and transport[2-4] properties of semiconductors, little is known about them either experimentally or theoretically. For example, absorption (and luminescence) in indirect-gap semiconductors proceeds via two scattering mechanisms involving e-ph as well as h-ph interactions. The intensity of a given transition is proportional to the square of the sum of terms involving e-ph and h-ph matrix elements, $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$, respectively, and hence is strongly affected by the constructive or destructive interference that can occur between the two mechanisms. Despite nearly three decades of research into processes which involve e-ph and h-ph interactions, the matrix elements ($S_{\text{e-ph}}$ and $S_{\text{h-ph}}$) were never explicitly evaluated. Recent piezospectroscopic studies of the fundamental absorption edges in Si (Ref. 5) and GaP (Ref. 6) have yielded the magnitudes and phases of the e-ph and h-ph matrix elements for the TO (Γ-Δ) phonon process in Si, and the LA and TA (Γ-X) phonons of GaP.[1] However, to date there has been no theoretical effort in this area.

In this Letter, we present the first theoretical calculation of the magnitudes and phases of $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$ for the TO, LO, TA, and LA indirect-phonon-assisted (Γ-Δ) transitions in Si. We have used the "rigid-ion" model to represent the interactions, as well as pseudopotential wave functions and form factors ($V_{\vec{q}}$) for the potential (the "rigid-pseudoion" model[7]). Within the context of the model, this was a first-principles calculation.

For the TO phonon, our results are in excellent agreement with the experimental values in both magnitude and phase. In addition, using the calculated numbers for $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$ for the various phonons, we have correctly accounted for the relative as well as absolute intensities of all four phonon-assisted indirect transitions in

Si. The successful description of the indirect spectrum provides a rigorous test of the model, since the intensities are critically dependent on both the magnitudes and phases of the matrix elements. Previous applications of the rigid-pseudoion model in calculating equivalent intervalley deformation potentials in PbTe and SnTe,[8] electron-phonon (intervalley and intravalley) coupling constants in graphite,[3] and the temperature dependence of the direct gap of Ge,[7] as well as PbTe and PbSe,[9] did not provide a complete test of the model. In these studies only the magnitudes of $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$ were obtained and in the last three cases averages over various scattering mechanisms were performed.

In the "rigid-ion" model, the e-ph (h-ph) interaction Hamiltonian is given by[8,9]

$$\mathcal{H}_l = \sum\nolimits_{j,\beta} \delta\vec{R}_{j,\beta} \cdot \nabla V(\vec{r} - \vec{R}_{j,\beta}{}^0), \tag{1}$$

where $V(\vec{r} - \vec{R}_{j,\beta}{}^0)$ is the potential about the atomic core in its equilibrium position $\vec{R}_{j,\beta}{}^0$ with lattice and basis indices j and β, respectively. $\delta\vec{R}_{j,\beta}$ is the displacement of the βth atom from equilibrium and l is the phonon mode. Within the framework of the rigid-pseudoion model, the matrix elements of $\mathcal{H}_l$ for diamond-type materials can be expressed as[7]

$$S_{\text{e-ph}_l} = \langle \varphi_{\vec{k}',s'} | \mathcal{H}_l | \varphi_{\vec{k},s} \rangle$$

$$= i\left[\frac{\hbar}{2M\omega_l(\vec{Q})}\right]^{1/2} \sum_{\vec{G},\vec{G}'} (C_{\vec{G}+\vec{G}'}{}^{\vec{k}',s'})^*(C_{\vec{G}'}{}^{\vec{k},s}) V_{\vec{Q}-\vec{G}}(\vec{Q}-\vec{G}) \cdot (\hat{\sigma}_{+,l}\cos\vec{G}\cdot\vec{\tau} + \hat{\sigma}_{-,l}\sin\vec{G}\cdot\vec{\tau}), \tag{2}$$

where $\varphi_{\vec{k}',s'}$ and $\varphi_{\vec{k},s}$ are the final and initial scattering states, respectively, $\vec{k}$ ($\vec{k}'$) and s (s') are wave vectors and band indices, respectively. For hole scattering h-ph_l replaces the subscript e-ph_l. In Eq. (2), $\vec{Q}$ is the wave vector of a phonon of the lth branch having a frequency $\omega_l(\vec{Q})$ with "in-phase" and "out-of-phase" polarization vectors $\hat{\sigma}_{+,l}$ and $\hat{\sigma}_{-,l}$, respectively. These eigenvectors are related to the polarization vectors of the two atoms of the basis through a unitary transformation.[7,10] M is the mass of an atom of the basis, $\vec{\tau} = (a_l/8)(1,1,1)$ is a basis vector where a_l is the lattice constant, $\vec{G}$ and $\vec{G}'$ are reciprocal lattice vectors, $V_{\vec{Q}-\vec{G}}$ is a pseudopotential form factor, and $C_{\vec{G}'}{}^{\vec{k},s}$ is the expansion coefficient of the pseudo plane-wave representation of $\varphi_{\vec{k},s}$. Equation (2) can readily be adapted for use with zinc-blende (or other) crystal structures.

We have evaluated Eq. (2) by using a 67-plane-wave expansion for the wave function and a local pseudopotential form factor $V_{\vec{q}}$ in the range $V_{0.85} < V_q < V_5$. $V_{\vec{q}}$ was interpolated through the values of Pantelides,[11] which were used in the calculation of electronic structure. Our interpolation is shown in Fig. 1. The phonon polarization vectors were obtained from a second–nearest-neighbor "shell-model" calculation which utilized experimentally determined phonon frequencies at $\vec{k}=0$ and the Brillouin zone edge at the X point.[10] These eigenvectors were found to be within 2% of those derived from the more exact Weber bond-charge model.[12] This indicates that the polarization vectors are most likely model independent and therefore not a significant source of error in our calculation. Thus, within the context of the model, the pseudo wave functions and interpolation of $V_{\vec{q}}$ are the major sources of uncertainty.

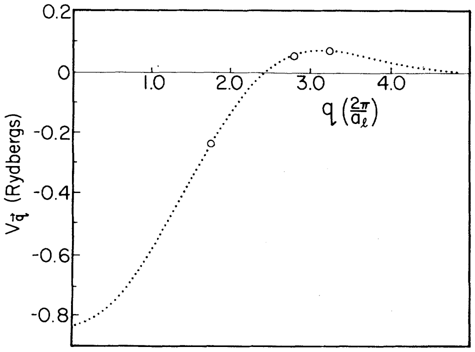

FIG. 1. The interpolation of the local pseudopotential form factor, $V_{\vec{q}}$, for Si. The open circles are the values of Ref. 11.

TABLE I. Theoretical values (in units of 10^{-3} Ry) of $S_{\text{e-ph}}$ and $S_{\text{h-ph}}$ for the TO, LO, TA, and LA ($\Gamma-\Delta$) phonons of Si. Also listed are the experimental values from Ref. 1 for the TO phonon. The conduction-band intermediate states are $\Gamma_{2,c}{}'$ for the LO phonon and $\Gamma_{15,c}$ for the others. $\Delta_{5,v}$ is the intermediate valence-band state for all of the phonons.

	TO				
Phonon (l)	Theory	Expt.	LO	TA	LA
$S_{\text{e-ph}}$	$+19^{a}$	15.3 ± 2.3^{a}	-13	-2.0	$+23$
$S_{\text{h-ph}}$	-24^{a}	-18.7 ± 2.8^{a}	-36	$+7.0$	$+25$

[a] Ref. 1

Listed in Table I are the results of our calculation of $S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ for the four Γ-Δ phonons in Si, together with the experimental values for the TO phonon. The theoretical and experimental values for the TO case are in excellent agreement in both magnitude and phase. The sign of the ratio $S_{\text{e-ph}_l}/S_{\text{h-ph}_l}$ is fixed. However, $S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ have an arbitrary common phase factor. We have chosen this phase factor such that $S_{\text{e-ph}_{\text{TO}}}$ is real and positive, and thus $S_{\text{h-ph}_{\text{TO}}}$ is real and negative.

A further test of the model is the correct description of the relative as well as absolute intensities of the indirect transitions of Si. The absorption coefficient $\alpha_l(\omega)$ of an indirect-gap material, resulting from an electronic transition between states differing in energy by E_g and accompanied by the creation or annihilation of a phonon of the lth branch, is given by[1]

$$\alpha_l(\omega)=Af_l\{L(\hbar\omega-E_g\mp\hbar\omega_l(\vec{Q}))/\hbar\omega\}, \tag{3}$$

where $\hbar\omega$ is the phonon energy, $L(\hbar\omega-E_g\mp\hbar\omega_l(Q))$ is a line-shape factor where the ∓ refers to phonon emission and absorption, respectively. The frequency-independent term, Af_l, is proportional to the "strength" of the transition. At low temperature only phonon emission is observed because $n_Q\approx 0$, where n_Q is the phonon occupation number. In Eq. (3) A is a density-of-states constant involving certain materials parameters, i.e., index of refraction, electron and hole effective masses, etc. Both A and L depend upon whether excitons or free electron-hole pairs are formed. In Eq. (3) f_l is the "oscillator strength" of the indirect transition and is proportional to the square of sums of terms involving the product of $S_{\text{e-ph}_l}$ (and $S_{\text{h-ph}_l}$) with an optical matrix element divided by an energy difference between the initial and final (e-ph or h-ph) scattering states. Complete expressions for A and f_l are given in Ref. 1.

We have evaluated f_l for each of the Γ-Δ phonon-assisted processes of Si by using (a) the theoretical values of $S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ listed in Table I, (b) optical matrix elements obtained from $\vec{k}\cdot\vec{p}$ calculations,[13] and (c) experimentally determined values of the energy differences.[14] From these results, we have calculated the product Af_l, for the case of exciton formation. Listed in Table II are both theoretical and experimental values of Af_l.

The overall agreement between theory and experiment is quite good. The theoretical values are somewhat larger than the experimental ones. This result is due to the fact that any uncertainty in the values of $S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ will produce an uncertainty twice as large in the term Af_l. In addition to this, the coefficient A of Eq. (3) was derived on the basis of a simple Bohr model for the exciton and thus it also may be a source of some uncertainty.[1] Also listed in Table II are the experimental and theoretical values of Af_l normalized to Af_{TO}. In this case the agreement between theory and experiment is very good. These results are an important confirmation of the validity of our model.

A significant consequence of our calculation lies in explaining the mechanisms responsible for the intensities of the Γ-Δ indirect transitions of Si. In the following discussion, we will show that a delicate balance between the phases and magnitudes of the e-ph and h-ph matrix elements is responsible for the relative strengths of these transitions. From Table I we see that constructive interference ($S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ opposite in sign) is responsible for the dominance of the TO phonon. Although the TA phonon also exhibits constructive interference it is weak because

TABLE II. Experimental and theoretical values (in units of $10^{-9}(\mathcal{R}^{1/2}a_0^{-1})$) of the coefficient, Af_l [see Eq. (3)], for the TO, LO, TA, and LA (Γ − Δ) phonons of Si. Also listed are the experimental and theoretical values of Af_l normalized to strength of the TO phonon.

	TO		LO		TA		LA	
Phonon (l)	Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory
Af_l	21.8[a] 26.9[b]	37.0	3.23[a]	5.2	0.638[a] 0.723[b]	1.2	⋯[c]	0.63
Af_l/Af_{TO}	1.0[a,b]	1.0	0.15[a]	0.14	0.0292[a] 0.0270[b]	0.032	⋯[c]	0.017

[a] Ref. 15.

[b] Ref. 16.

[c] The LA transition is so weak that it is not observed experimentally.

$S_{\text{e-ph}_{\text{TA}}}$ and $S_{\text{h-ph}_{\text{TA}}}$ are considerably smaller in magnitude than the e-ph and h-ph matrix elements of the other phonons. For both the LO and LA phonons the e-ph and h-ph scattering interfere destructively. In the case of the LA phonon, the transition is very weak despite the fact that the magnitudes of $S_{\text{e-ph}_{\text{LA}}}$ and $S_{\text{h-ph}_{\text{LA}}}$ are not small. The ratio $S_{\text{e-ph}_{\text{LA}}}/S_{\text{h-ph}_{\text{LA}}}$ is such as to cause almost complete destructive interference. On the other hand, for the LO phonon, $S_{\text{e-ph}_{\text{LO}}}/S_{\text{h-ph}_{\text{LO}}} = 0.36$ and thus the effect of destructive interference is reduced. From the above discussion, we see that accounting for the relative (as well as absolute) intensities provides a delicate test of the model, i.e., the calculation must yield the correct magnitudes and phases of $S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ for *each* Γ-Δ transition Si.

Since the form factors used in evaluating $S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ are interpolations of those employed in band-structure calculations, the rigid-pseudoion model may provide a tool for testing various analytic forms of the pseudopotential. In our study we used several analytic forms of $V_{\vec{q}}$ and found that the magnitudes of the matrix elements changed by as much as 15% and the values of Af_l varied by almost 30%. However, the normalized values of Af_l were not as sensitive.

In conclusion, using the rigid-pseudoion model, we have calculated $S_{\text{e-ph}_l}$ and $S_{\text{h-ph}_l}$ for the Γ-Δ phonon-assisted transitions of Si. Consequently, we now have a complete understanding of the mechanisms governing the indirect absorption of this material. By correctly accounting for relative as well as absolute strengths of the indirect transitions in Si, we have rigorously demonstrated the validity of the rigid-pseudoion model in calculating e-ph and h-ph matrix elements in this material. Therefore, the model shows great promise in dealing with a variety of intervalley scattering processes in diamond and zinc-blende materials as well as in other semiconductors. Finally, the model may serve as a test for various analytic forms of the pseudopotential.

We wish to express our thanks to Dr. M. L. Cohen, Dr. S. Pantelides, Dr. M. Schlüter, and Dr. P. B. Allen for useful discussions and Dr. G. Wright for his encouragement. This research was supported by U. S. Office of Naval Research Contract No. N00014-78-C0890.

---

[1] O. J. Glembocki and F. H. Pollak, Phys. Rev. B, to be published, and references therein.

[2] See, for example, B. R. Nag, *Electron Transport in Compound Semiconductors* (Springer-Verlag, New York, 1980).

[3] T. Inoshita and H. Kamimura, Synth. Met. 3, 223 (1981).

[4] P. N. Butcher and W. Fawcett, Proc. Phys. Soc. London 86, 1205 (1965).

[5] F. H. Pollak, A. Feldblum, H. D. Park, and P. E. Vanier, Solid State Commun. 28, 161 (1978).

[6] O. J. Glembocki and F. H. Pollak, Phys. Rev. B, to be published.

[7] P. B. Allen and M. Cardona, Phys. Rev. B 23, 1495 (1981).

[8] M. L. Cohen and Y. W. Tang, *Proceedings of the Conference on the Physics of Semi-metals and Narrow-Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 303.

[9] M. Schlüter, G. Martinez, and M. L. Cohen, Phys. Rev. B 12, 650 (1975).

[10] M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Wiley, New York, 1974).

[11] S. T. Pantelides, private communication; J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. B 21, 3545 (1980).

[12] P. B. Allen, private communication; W. Weber, Phys. Rev. B 15, 4789 (1977).

[13] M. Cardona and F. H. Pollak, Phys. Rev. 142, 530 (1966).

[14] J. S. Kline, F. H. Pollak and M. Cardona, Helv. Phys. Acta 41, 968 (1968).

[15] P. J. Dean, Y. Yafet, and J. R. Haynes, Phys. Rev. 184, 837 (1969).

[16] G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. 111, 1245 (1958).