

Inter-valence-band electronic Raman scattering due to photoexcited holes in $\text{Ge}_{1-x}\text{Si}_x$

Elena Nazvanova and Tohru Suemoto

The Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

Shoichi Maruyama and Yukio Takano

Science University of Tokyo, Faculty of Industrial Science and Technology, Yamazaki 2641, Noda-shi, Chiba 278, Japan

(Received 28 December 1999)

The inter-valence-band electronic Raman scattering (IVRS) corresponding to the hole excitation from the heavy hole to light hole band has been studied in the bulk $\text{Ge}_{1-x}\text{Si}_x$ alloys for $0 < x < 0.14$. The measured Stokes energy shift depends on the energy of the incident photons, and also on the alloy compositions. This behavior is successfully explained invoking the resonant interband hole transitions at selected locations in the Brillouin zone caused by the incident photons. The origin of the band width of the IVRS band is discussed in terms of lifetime broadening and momentum uncertainty during the resonant scattering process.

I. INTRODUCTION

The manipulation of semiconductor materials by the growth of their alloys and superstructures leads to new and sometimes unexpected semiconductor properties. Examples are the enhanced mobility and the appearance of new direct optical transitions in strained Si-Ge superlattices. Silicon and germanium form a continuous series of solid substitutional solutions in all proportions.¹ $\text{Ge}_{1-x}\text{Si}_x$ alloys have attracted much revived attention because of their high potential for a device application such as “quasi-direct-gap” photodetectors and staircase-avalanche photodetectors. When Si-Ge mixed crystal is used as a substrate for the epitaxial growth of Ge-Si superlattices, reduction of the stress due to lattice mismatching is expected. Although the valence and conduction bands of the most important semiconductors are well understood by now, our knowledge of the band structures of their mixed crystals and strained lattices is still qualitative, especially in the regions away from the zone center.

Raman scattering has long been known as a powerful tool for characterization of electronic as well as the structural and vibrational properties of bulk semiconductors and also nanostructural and heterostructured semiconductors.² Owing to the tunability of the incident photon energy, the resonant electronic Raman measurement provides additional information, that is, selectivity in the momentum space in exploiting the electronic band structures.

The inter-valence-band Raman scattering (IVRS) originates from an electron transition from its initial energy state in one of the valence bands to another state via an intermediate state in the conduction band. Thus the Raman shift corresponds to the energy difference between these two valence bands. This Raman band has been studied in the heavily doped semiconductors,^{3–5} and in Ge.^{6,7} In this report, we present a study of the IVRS in the bulk Ge-Si alloys and propose the use of IVRS as a tool for the band structure investigation in this system.

II. EXPERIMENT

We investigated $\text{Ge}_{1-x}\text{Si}_x$ bulk crystals with x varying from 0 to 0.14. Polycrystalline ingots were grown by the

liquid-encapsulated Bridgman method with CaCl_2 as an encapsulant⁸ and the samples were cut from that ingot, polished by alumina polishing suspensions and etched with a diluted hydrofluoric acid. As the growth of Ge-Si monocrystals of a uniform concentration is rather complicated, we used a portion of the ingot with a reasonable compositional gradient across the surface. We applied a coating on the polished $1 \text{ cm} \times 1 \text{ cm}$ sample surface by a mask of a photoresist (Positive S1400-S1800 series Photoresist, SHIPLEY), so the whole surface was mapped by grids into 200 cells with a dimension of $0.5 \text{ mm} \times 1 \text{ mm}$. Therefore, we have got 200 “different samples” on a piece of one ingot with a definite composition determined sequentially by EPMA (electron probed micro-analysis) method.

Raman measurements have been performed in a quasi-back-scattering geometry at room temperature. A tunable cw Ti:sapphire laser (TSL300, Showa Optronics) and a ring Rh6G-dye laser (Coherent CR-699) were used for excitation. The background fluorescence of the lasers was suppressed by a filter stage optics consisting of a prism and a slit. The laser light was focused on the sample surface by a spherical achromatic lens ($f=30 \text{ mm}$) to a spot of $30\sim 50 \mu\text{m}$ diameter. Owing to the long lifetime of carriers due to indirect-gap nature of Ge, the carrier density reaches a rather high level even under a cw excitation. The estimated density of the photoexcited holes was about $5 \times 10^{17} \text{ cm}^{-3}$ under the excitation power of 150–170 mW, assuming the electron generation efficiency by one photon to be unity, and the same values of a diffusion constant and a lifetime of holes as in Ref. 7. The estimated heating of the samples was about 30 K at room temperature.

The maximum composition gradient across the sample surface is estimated to be 2.2%/mm from our mapping data, and the composition uncertainty within the $50 \mu\text{m}$ laser spot will then be less than $\pm 0.06\%$. The accuracy of the absolute composition depends also on the positioning error of the laser spot to the center of the cell. The error limit is estimated to be $\pm 0.17\%$, corresponding to the positioning error of $\pm 75 \mu\text{m}$.

Raman spectra have been recorded by a single monochromator (SPEX 270 M, $f=27 \text{ cm}$) equipped with a liquid-

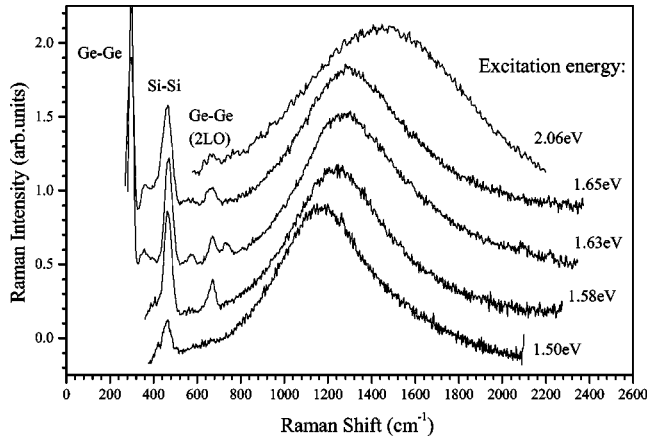


FIG. 1. Raman spectra of $\text{Ge}_{1-x}\text{Si}_x$ ($x=0.075$) measured with various excitation energies at room temperature.

nitrogen-cooled CCD camera (SPEX) and super notch filters (Kaiser Optical Systems). The spectral resolution of the system was about 1 nm corresponding to $\sim 15 \text{ cm}^{-1}$ at 800 nm. The experimental spectra were corrected for the instrumental spectral response. The intensity of the IVRS spectra in crossed polarization configuration was slightly larger than that in parallel polarization. However, the shape and the position of the band were independent of the polarization. Therefore, the spectra were always taken in nearly parallel polarization during the measurements.

III. RESULTS

Typical Stokes spectra of Ge-Si alloy with 7.3 at. % of Si recorded at room temperature for different incident photon energies are shown in Fig. 1. The ordinate in the plot is proportional to the photon counting rate per unit energy interval.

The prominent Raman-active peaks positioned at around 300, 390, and 480 cm^{-1} are attributed to the vibrations of Ge-Ge, Ge-Si, and Si-Si neighboring pairs,^{9,10} respectively. Their two-phonon replicas are found in the range from 600 to 800. In addition to these features, the broad structures were observed in the 900–1600 cm^{-1} region on the Stokes side of the emission. The shift of the structure becomes larger with increasing the incident photon energy. A similar behavior was already found in p -, n -doped, and intrinsic Ge (Refs. 7,11) and this band has been assigned to an inter-valence-band transition of the photogenerated holes.

Typical spectra for a given photon energy (1.65 eV) in alloys with different Si concentrations are shown in Fig. 2. When the Si concentration increases, decrease of Stokes shift is observed. When the concentration exceeded about 15 at. %, this broad structure overlaps with the intensive LO-phonon related lines and becomes indistinguishable.

IV. DISCUSSION

We have plotted their Stokes shifts in Fig. 3 for different Si concentrations as a function of the laser frequency. In all the samples, we can see the following aspects. (i) The Raman shifts increase as the photon energy increases. (ii) They converge to similar values at 2.06 eV. (iii) The slope of the

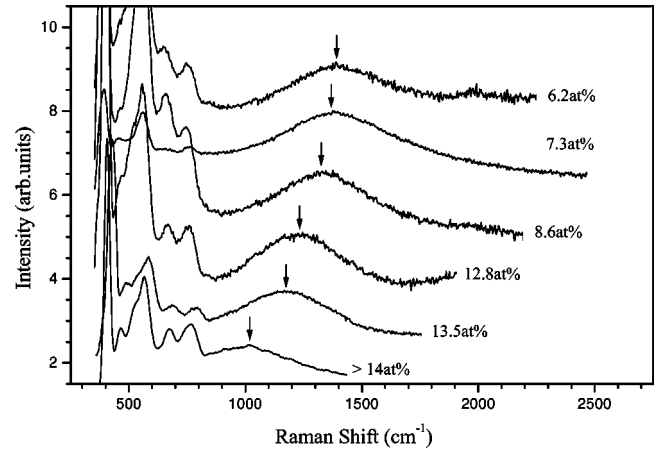


FIG. 2. Raman spectra of $\text{Ge}_{1-x}\text{Si}_x$ for various x under 1.65 eV excitation measured at room temperature. The arrows show the peak positions of the IVRS band.

photon energy dependence increases as the Si concentration increases.

The energy dispersion curves of holes in Si-Ge alloys were calculated in a way similar to Lawaetz's calculation of Ge energy band structure.¹² After Lawaetz, the energy spectra of the heavy-hole and light-hole bands [$E_h(k)$, $E_l(k)$] can be calculated analytically to the second order in k for two special directions in k space: $\langle 100 \rangle$ and $\langle 111 \rangle$. For the $\langle 100 \rangle$ direction we have¹²

$$E_h(k) = -(A - B)k^2, \quad (1)$$

$$E_l(k) = -\frac{1}{2}[(2A + B)k^2 + \Delta] + \left\{ \frac{1}{4}[(2A + B)k^2 + \Delta]^2 - \Delta(A + B)k^2 - (A + 2B)(A - B)k^4 \right\}^{1/2}, \quad (2)$$

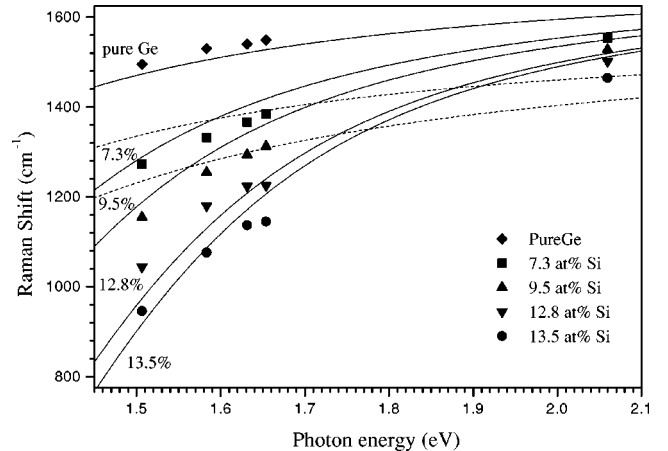


FIG. 3. Composition and photon energy dependence of the peak frequencies of the IVRS band. The symbols correspond to experimental results. The broken curves show the calculated results for $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. The uppermost curve corresponds to pure Ge for $\langle 111 \rangle$ but shifted for $+135 \text{ cm}^{-1}$. The solid curves are calculated results for $\langle 111 \rangle$ direction shifted for $+135 \text{ cm}^{-1}$. See text for the detail.

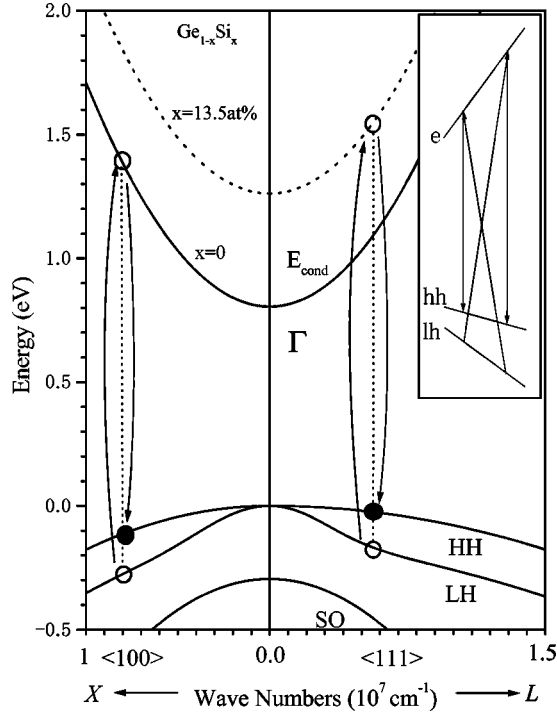


FIG. 4. The calculated band structure of $\text{Ge}_{1-x}\text{Si}_x$ and resonant Raman processes. The solid curves correspond to pure Ge ($x=0$) and the broken curve shows the conduction band for $x=0.135$. The inset shows slightly nonvertical transitions in resonance with the incident photons.

where $A = 13.27 \pm 0.025$, $B = 8.63 \pm 0.12$, $|C| = 12.4 \pm 0.25$ in units of $\hbar/2m$, and m is the free electron mass. For the $\langle 111 \rangle$ directions, B is replaced by $D/\sqrt{3}$, where $D = (3B^2 + C^2)^{1/2}$.

The energy spectrum of the conduction band is given in parabolic approximation by

$$E_c(k) = Ek^2 + E_{\text{gap}}, \quad (3)$$

where E_{gap} is the direct gap at the Γ point and is equal to 0.805 eV at $T=300$ K and $E=23.8$ in units of $\hbar/2m$. We suppose that the incorporation of Si into Ge matrix in Si-Ge alloy only slightly affects the band structure of Ge, so it remained Ge type. Thus we assumed this influence to be represented simply by change of the direct band gap

$$E_{\text{gap}} = 0.805 + 3.38x/100, \quad (4)$$

where x is the Si concentration in atomic percents.¹³

The calculated band structures for $\text{Ge}_{1-x}\text{Si}_x$ are shown in Fig. 4 for $\langle 100 \rangle$ and $\langle 111 \rangle$ directions in k space. While the valence bands shown by the solid curves are common for all values of x , and the conduction bands displayed by solid and broken curves correspond to those for $x=0$ at.% and $x=13.5$ at.%, respectively. The resonant IVRS processes for $\hbar\omega_{\text{incident}} = 1.63$ eV are depicted in the figure by upward and downward arrows. This process involves excitation of an electron from the light- to the heavy-hole band via an intermediate state in the conduction band, resulting in scattering of the corresponding hole from the heavy-hole to the light-hole band. In this process, the increase of the photon energy should result in the increase of the Stokes shift, as was ob-

served in experiments. Another possible resonant IVRS process is the excitation of an electron from the split-off band through an intermediate state in the conduction band and its deexcitation into the HH band. But this process is hardly relevant to our experimental situation, since the resulting Stokes shift should be much larger than 2000 cm^{-1} .

The Raman spectrum in this model is given by

$$I(\Delta\omega) \propto \sum_{i,f} P(E_i) \delta\left(\frac{E_i(\vec{k}) - E_f(\vec{k})}{\hbar} - \Delta\omega\right) |\vec{e}_2(R)\vec{e}_1|^2, \quad (5)$$

$$(R)_{\mu\nu} = \frac{1}{m} \sum_n \frac{\langle f|\hat{p}_\mu|n\rangle \langle n|\hat{p}_\nu|i\rangle}{\hbar\omega_{\text{incident}} - [E_n(\vec{k}) - E_i(\vec{k})] + i\Gamma}, \quad (6)$$

where $\Delta\omega$ is the Raman shift, $|i\rangle$, $|n\rangle$, and $|f\rangle$ are the wave functions of the multiparticle system in initial, intermediate and final states, and the energies of these states are denoted by $E_i(\vec{k})$, $E_n(\vec{k})$, and $E_f(\vec{k})$. In the intermediate state, we have an excited electron in the conduction band, an hole left behind in the LH band, and thermally populated holes in the HH band. Neglecting the nonresonant terms in Eq. (6) and assuming k -conserving transitions, the Raman shift $\Delta\omega_0$ can be estimated as

$$\Delta\omega_0 = \sum_{k_A} P_{k_A} \frac{E_l(\vec{k}_A) - E_h(\vec{k}_A)}{\hbar}, \quad (7)$$

where P_{k_A} is the normalized weighting function reflecting $f_h(1-f_l)|M_{k_A}|$. $|M_{k_A}|$ contains the matrix element of this transition, $f_h(E_h)$, $f_l(E_l)$ are the distribution functions of holes in the HH and LH bands, and \vec{k}_A is a solution of the equation

$$\hbar\omega_{\text{incident}} = E_c(\vec{k}) - E_l(\vec{k}). \quad (8)$$

If we had non- k -conserving (indirect) transitions involving the Fermi surface in the heavy-hole band, the Raman shift should decrease at higher excitation power corresponding to the lowering of the Fermi level. However, such dependence was never observed, so we rejected the possibility of an indirect resonance and assumed the k -conserving transitions.

The dependence of Raman shift $\Delta\omega$ on the incident photon energy for the pure Ge was calculated for $\langle 100 \rangle$ and $\langle 111 \rangle$ directions and shown in Fig. 3 by broken lines. Although the tendency of the experimental data is well reproduced, the absolute values of the calculated Raman shifts for these two directions are smaller than experimental values.

As was already mentioned, the Kane's calculations have shown¹⁴ that the energy difference between the LH and HH bands has a maximum in $\vec{k}||\langle 111 \rangle$ directions, and a minimum in $\vec{k}||\langle 100 \rangle$, while the energy gap between LH and conduction bands is the smallest in $\vec{k}||\langle 111 \rangle$ direction. Therefore, all the possible values of Raman shift are expected to lie in the definite range from the smallest one for the holes with $\vec{k}||\langle 100 \rangle$, to the largest—for the holes with $\vec{k}||\langle 111 \rangle$, i.e., between these two curves.

As the hole population in the light hole band will be negligibly small under steady state excitation, the intensity of

IVRS will reflect the hole density in the heavy hole band. Assuming the Boltzmann distribution for heavy holes at room temperature, we estimated a ‘‘center of gravity’’ for the Raman shift from a ratio

$$\exp\left(\frac{E_h(\vec{k}_A|\langle 111 \rangle)}{k_B T}\right) / \exp\left(\frac{E_h(\vec{k}_A|\langle 100 \rangle)}{k_B T}\right). \quad (9)$$

This ratio gives a value of 10 for a resonant condition at 1.5 eV excitation, and 77 for a resonance at 2.06 eV, which means the difference in the efficiency of Raman scattering for the holes with $\vec{k}|\langle 111 \rangle$ is about 1–2 orders of magnitude larger than that for holes with $\vec{k}|\langle 100 \rangle$. Thus we can expect that the ‘‘center of gravity’’ should practically be located on the curve calculated for $\langle 111 \rangle$ direction.

We have still a discrepancy more than 150 cm^{-1} . However, it does not seem too large, considering the rather large width of the Raman band ($400\text{--}500 \text{ cm}^{-1}$). Furthermore, the calculation based on the $k \cdot p$ method may not be very accurate, because relevant k is as large as one tenth of the Brillouin zone. Therefore, we shifted the curve for $+135 \text{ cm}^{-1}$ to get a better agreement with the experiment as shown by a solid curve for $\langle 111 \rangle$. The dependence of Raman shift $\Delta\omega$ on the incident photon energy for other Si concentrations was calculated and shown in the same figure by solid curves, which are shifted with the same amount $+135 \text{ cm}^{-1}$. All the important features (i) to (iii) are reproduced quite satisfactorily. The relatively large deviation at 2.06 eV is again ascribed to the inaccuracy of the calculation, because the relevant k is even larger.

This IVRS band has an extremely large bandwidth (about 500 cm^{-1} for excitation photon energies from 1.50 to 1.65 eV), and it exceeds 700 cm^{-1} for 2.06 eV. As mentioned in Sec. II, the composition deviation within the laser spot is less than $\pm 0.06\%$, which gives an additional broadening of 7.7 cm^{-1} for 1.5 eV excitation, according to the calculated composition dependence of the Raman shift shown in Fig. 3. Since this value is far smaller than the observed Raman bandwidth itself, this cannot be the origin of the large band width. We can suppose several origins for the band broadening: (1) Contribution from the transitions at various k in the Brillouin zone, (2) effect of disorder, and (3) lifetime broadening. Although the contribution (1) has been suggested as one of the reasons for the broadening in Ref. 7, this cannot be larger than the $\langle 111 \rangle$ - $\langle 100 \rangle$ splitting, which is only 100 cm^{-1} as seen from the dash-dot curves in Fig. 4 and is not enough to explain the observed width. Effect of (2) does not seem to be important, because there is no indication of the increase of the width in Si-doped samples compared to the pure Ge. The charged defects have been shown to have no effect on the band width.⁷ In the following, we will discuss the effect of (3) in some detail. When the resonant Raman process occurs among discrete three levels, the band width of the Raman spectrum is determined by the lifetime broadening of the initial and the final states:

$$\Gamma_l + \Gamma_h.$$

However in the present case, initial, intermediate and final states are continuously distributed and the Raman band width depends also on the selectivity of the set of energy

levels contributing to the light scattering process. As a consequence of the finite lifetime of the carriers, the mean free path of the carrier will have a finite value. This brings about a wave vector uncertainty. Therefore, we cannot assume strict vertical transitions in the resonance process with the incident light. The uncertainty in the wave vector is given by $\Delta k = 1/(\tau v_g) = (\partial k / \partial \omega) \Gamma$, where v_g is the group velocity and Γ is the lifetime broadening of the relevant carriers. Considering this effect for the light holes and the conduction electrons, we can expect slightly nonvertical transitions as shown in the inset of Fig. 4. The contribution to the band width from this effect is

$$\Delta k(v_{gl} + v_{gh}) = (\Gamma_l + \Gamma_e) \left[1 + \left(\frac{\partial \omega_h}{\partial k} \right) \left(\frac{\partial k}{\partial \omega_l} \right) \right]. \quad (10)$$

If the heavy hole mass is sufficiently larger than that of the light hole, we can neglect the second term in Eq. (10), and the total band width is given by

$$\Gamma_{tot} = 2\Gamma_l + \Gamma_h + \Gamma_e. \quad (11)$$

As for the electrons, it has been shown that most electrons are initially scattered to the X valleys with a rate greater than 10^{13} sec^{-1} , even though they ultimately relax to the lower-energy L valleys.¹⁵ They are scattered into the X valleys, relax there, and are scattered from there to the L valleys in 1 ps range.

According to the cooling time of the heavy holes obtained from a transient Raman scattering experiment,¹⁶ the phonon emission rate of the hot heavy hole is in the order of 100 fs. Although very little is known about the time scale of the relaxation of the light holes, we can assume a similar value as heavy holes. As a rough estimation, we assume 100 fs for each carrier [which gives a Lorentzian band width (FWHM) of 106 cm^{-1}] and sum up these widths following Eq. (11). Then we obtain 424 cm^{-1} , which is close to the observed band width.

The carrier lifetime is shorter at positions E sufficiently above the conduction band edge (or below the valence band edge) provided that most levels below are unfilled. Because the carrier-LO-phonon scattering probability is proportional to the density-of-states (DOS) of the final state of a scattering process, and the DOS is in proportion to \sqrt{E} . Thus we can qualitatively understand the larger band width observed at 2.06 eV excitation.

V. CONCLUSIONS

The inter-valence-band Raman scattering has been reported for $\text{Ge}_{1-x}\text{Si}_x$ alloys with x ranging from 0 at. % to about 15 at. % and for the incident photon energies from 1.46 to 2.06 eV. The comparison to a calculation based on the $k \cdot p$ method showed very good agreement in the tendency of excitation energy dependence and in the compositional dependence.

ACKNOWLEDGMENTS

The authors would like to thank Professor A. Kotani for helpful discussions. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

- ¹Vipin Shivastava and S.K. Joshi, Phys. Rev. B **8**, 4671 (1973).
- ²Zhou Xingjiang, M. Cardona, D. Coldon, and V. Viallet, Physica C **282-287**, 1013 (1997).
- ³D. Olego, M. Cardona, and U. Rossler, Phys. Rev. B **22**, 1905 (1980).
- ⁴M.A. Kanehisa, R.F. Wallis, and M. Balkanski, Phys. Rev. B **25**, 7619 (1982).
- ⁵J. Wagner and M. Cardona, Phys. Rev. B **32**, 8071 (1985).
- ⁶D.L. Mills, R.F. Vallis, and E. Burstein, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p.107.
- ⁷K. Tanaka, H. Ohtake, and T. Suemoto, Phys. Rev. B **50**, 10 694 (1994).
- ⁸K. Kadokura and Y. Takano, J. Cryst. Growth **171**, 56 (1997).
- ⁹D.W. Feldman, M. Ashkin, and James H. Parker, Jr., Phys. Rev. Lett. **17**, 1209 (1966).
- ¹⁰M.A. Renucci, J.B. Renucci, and M. Cardona, in *Proceedings of the Second International Conference on Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 326.
- ¹¹K. Tanaka, H. Ohtake, and T. Suemoto, Phys. Rev. Lett. **71**, 1935 (1993).
- ¹²P. Lawaetz, Phys. Rev. **174**, 867 (1968).
- ¹³J.S. Kline, F.H. Pollak, and M. Cardona, Helv. Phys. Acta **41**, 968 (1968).
- ¹⁴E.O. Kane, J. Phys. Chem. Solids **1**, 82 (1956).
- ¹⁵X.Q. Zhou, H.M. van Driel, and G. Mak, Phys. Rev. B **50**, 5226 (1994).
- ¹⁶K. Tanaka, H. Ohtake, H. Nansei, and T. Suemoto, Phys. Rev. B **52**, 10 709 (1995).