THEORY ON OPTICAL PHONON MODES
AND RAMAN SCATTERING IN QUANTUM WELL SYSTEMS

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Bangfen Zhu
International Centre for Theoretical Physics, Trieste, Italy
and
Institute of Semiconductors, Chinese Academy of Sciences,
P.O. Box 912, Beijing 100083, People’s Republic of China *

ABSTRACT

On the basis of our recently reformulated expressions for the confined bulklike modes in quantum well systems, explicit expression for the Raman tensor associated with the various phonon modes in multiple quantum wells are derived. The results display systematically the selection rules as regards polarization configuration, phonon parity, and phonon scattering mechanisms. The microscopic theories have been worked out with both free electron–hole pairs and 2D–excitons as intermediate states. Specific features of these intermediate states are found to be of special importance for a quantitative theory. Thus heavy and light hole mixing effects, angular momentum state of the excitons can play a decisive role in determining the predominant scattering channels. Fröhlich interaction induced scattering, which is dipole allowed in multiple quantum wells, is shown to be related directly to barrier penetrations by the carriers and hole mixing. With this theory, explanations are provided related to such experiments as the resonant Raman profile, the effect of electric field on the Raman spectra, the lineshape of Raman spectra and the features of two–phonon Raman scattering in quantum well systems.

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* Permanent address.
1. INTRODUCTION

Since the 1980s, extensive investigations have been carried out on Raman scattering in quantum well systems, especially in GaAs/AlAs heterostructures. Through Raman scattering experiments, a basic understanding of the phonon structure in semiconductor superlattices was established: namely, as contrasted with the folding of the acoustic phonons, the confinement of the optical phonons to the corresponding constituent layers is compared to the quantized states in the "phonon quantum wells".

On the theoretical side, phonon modes of superlattices have been calculated on various models. The usually quoted analytical expressions for the mode potentials as well as the displacements are derived with the dielectric continuum model, which is also used to characterize the interface and the bulklike modes. With such phonon modes and one-component exciton states, selection rules as regards phonon symmetry, nature of electron-phonon interaction for different polarization schemes have been discussed by Enderlein et al. However, as noted first by Sood et al., the nodal structure of the confined bulklike modes based on the dielectric continuum model seems to be at variance with symmetry analysis as suggested by certain Raman scattering experiments. Besides, neglecting the mediated 2D-exciton structures as done in Ref.13 has lead to a lot of incorrect conclusions.

That a proper treatment of the Raman scattering in the multiple quantum wells (MQW's) is as yet not already available is not surprising, since it depends on a detailed understanding of the whole complexities of the phonon modes and electronic structure of superlattices, which received proper theoretical treatment only in the past few years. For example, just recently, after critically comparing the phonon modes derived from the dielectric continuum theory and a closely parallel microscopic model, Huang and Zhu have fully elucidated the implication of the light scattering data from the Cardona group and presented analytical expressions for the confined phonon modes in quantum wells. Another advance related to the theory of Raman scattering in the MQW's is the effect of heavy-(HH) and light hole(LH) mixing on the hole subbands, on the optical process and on the exciton states in these systems, which was not taken into proper consideration till 1984.
With such background, the present authors have recently presented a systematic microscopic theory on the optical phonon Raman scattering in multiple quantum wells mediated by free electron-hole pair\textsuperscript{20} and by excitons\textsuperscript{21} for various situations. In this paper, on the basis of our microscopic theory, we intend to present our main theoretical results on the resonant Raman profiles and Raman scattering spectra, demonstrating how the phonon eigenmodes and certain specific features of the intermediate states affect the scattering processes. Besides, we will give some insights into Raman experiments, such as the asymmetry between the incoming and outgoing resonant peaks, the selection rules on the second-order Raman scattering, etc.

2. OPTICAL PHONON MODES IN QUANTUM WELLS

Relatively realistic calculations of the phonon modes in superlattices have become available in recent years. However the use of such numerically calculated phonon modes would make the theoretical treatment of Raman scattering very unwieldy. The modes derived from the dielectric continuum model\textsuperscript{7}, though would be much more convenient to use, do not in fact correspond to the realistic modes, because the dielectric model by itself cannot provide a useful criterion for determining the eigenmodes in the superlattices. However, by following clues suggested by results of calculation with a "phonon quantum well" model\textsuperscript{15}, we were able to obtain following modified expressions for all the bulklike mode potentials, which apparently can be used in the role of Fröhlich interaction in superlattices.

\begin{equation}
\Phi_n(z) \propto \begin{cases}
\sin(\mu_n\pi z/d) + C_n z/d, & n = 3, 5, \ldots \\
\cos(n\pi z/d) - (-1)^{n/2}, & n = 2, 4, 6, \ldots
\end{cases}
\end{equation}

where $\mu_n$ and $C_n$ are constants, explicitly given in Ref. 15. As in the usual dielectric continuum treatment, the modified bulklike modes likewise vibrate with the bulk LO and TO frequencies and are confined to either one of the layers constituting the superlattice. According to (1), both the mode potential and the displacement functions of all the bulklike modes with nonzero parallel wave vector, $k_||$, have nodes at the interfaces. This means that both the electrostatic and the mechanical boundary conditions\textsuperscript{2-13} are required, namely, the correct boundary condition is the optical displacement function $\tilde{u}(\pm d/2) = 0$, where $d$ is the effective layer thickness.
It would seem that the microscopic results have missed a half-wavelength mode, \( n = 1 \). In fact, this is exactly how it should be. With \( k_{||} \) increasing from 0, the interface modes start off from \( \omega_{LO} \) and \( \omega_{TO} \) to move into the \( \omega_{LO} - \omega_{TO} \) gap. A close investigation shows that these are just the half-wavelength \( n = 1 \) modes moving away to become interface modes. So, the \( n = 1 \) mode in the macroscopic model should correspond to the interface mode (or Coulomb mode as named in Ref. 15) with zero \( k_{||} \) and in the dielectric model a mode with the longest wavelength repeatedly appears both as the \( n = 1 \) mode and the interface mode.

We have also extended our model to investigating optical phonon modes in 1D quantum wires. We have found that the above boundary conditions for the modes in 2D quantum well systems are also verified in 1D quantum wires, namely the appropriate boundary conditions for optical bulklike modes in 1D quantum wires is the vanishing displacement vector at the interfaces.

3. CERTAIN SPECIFIC FEATURES OF INTERMEDIATE STATES AND SELECTION RULES

With the explicit expressions given by Ref. 20, calculations of the Raman tensor has been carried out for various possible intermediate states (both the free electron-hole pairs and the discrete excitons) in a number of samples with the well widths ranging from 50\( \AA \) to 150\( \AA \). Generally speaking, the Raman process depends on the oscillator strengths of two intermediate states, on the electron-phonon interaction, and on the incident photon energy, which depend ultimately on the specific features of the intermediate states and the phonon modes.

3.1 Electron-Phonon Interaction

It is well known that there are two types of electron- optical-phonon interaction in semiconductor materials: deformation potential (DP) interaction and Fröhlich (F) interaction. As the electron-phonon interaction is in the nature of single-particle interaction, its matrix elements between the two intermediate states determinantal wave functions, can be straightforwardly worked out in terms of single-particle matrix elements, namely, the differences between the matrix elements of the electron scattering and that of the hole scattering.

The deformation potential interaction arises from the perturbation of the lattice periodic potential by the optical phonon modes. A long wavelength optical mode causes a "local" change in the lattice periodic potential, essentially the same as that due to a uniform relative displacement between the positive and negative ions. The DP interaction can be characterized by an integral average of the fast varying functions of the potential derivative over the relative displacement taken between the band-edge functions, resulting in the nondiagonal matrix elements.

As shown in (1), the LO modes are associated with an electrostatic field. By Fröhlich interaction, the LO modes can scatter either an electron or a hole. As in the present case the F-interaction, unlike the deformation potential, can be considered as slowly varying, so in the integration, the band edge functions only provide an orthogonality factor between distinct band edges. Thus, we can only obtain the diagonal matrix elements for F-process.
3.2 Exciton States

Since the discrete excitons play a decisive role in the optical process of the quantum wells, one should of course take into account the exciton effects in Raman scattering. Furthermore, the main difference between the electron-hole pair mediated and the exciton mediated Raman tensors is that the latter is a weighted electron-hole pair, but the selection rules are quite similar for both cases if an appropriate interpretation is made. Here we just comment on certain main features of the quasi-2D excitons.

The basic feature to be emphasised is the complex angular momentum structure of the quasi-2D excitons in quantum wells. Namely, the four hole-components of the exciton wave function are associated with different orbital angular momenta in the xy-plane representable as $\hbar(j - j_o)$, where $j_o$ just the label for the spinor-component with zero orbit angular momentum. The angular momenta of two intermediate discrete excitons play a decisive role in all three matrix elements in the Raman numerator:

(1). It can be readily proved that, out of 4-components of the exciton wave function, only the $j_o$ component contributes to the two photon interaction matrix elements. Usually, the s-excitons derived from two parity-matched subbands can make a dominant contributions to the optical transitions.

(2). The angular momenta of the two intermediate excitons also play a decisive role in the phonon scattering matrix element. With Fröhlich interaction, the scattering is nonvanishing only when $j_o$ for two excitons are equal. In other words, the angular momenta of the corresponding hole components of the two excitons must be completely matched. As contrasted to F- scattering, the DP interaction couples together hole components of the two excitons, which are relatively shifted by one ( for z- and y-displacements) or two ( for x-displacements) places. From this it follows that for nonvanishing scattering, the angular momenta associated with the hole components of the two excitons must be subject to such "shifted matching". In other words, for DP scattering by LO-modes( mainly z-displacements) we must have $j_o$ changed by 2 and for scattering by TO modes, we must have $j_o$ shifted by 1. Now if two intermediate states are both s-state excitons for strong resonance, the above requirements mean that the two excitons must separately be heavy and light hole excitons.

3.3 Allowed Fröhlich interaction induced Scattering

The Fröhlich interaction induced scattering is usually dipole forbidden in bulk materials because of cancellation between the electron's and the hole's contributions. But it is allowed in the quantum well systems within the dipole approximation. There are two separate cases: intersubband scattering ( i.e. the electron (or hole) of the two intermediate states are derived from different subbands) and intrasubband scattering. In the intersubband scattering event, only an electron or only a hole is scattered, so no cancellation occurs. As for intrasubband scattering, since
the penetration into the potential barrier for electron and for hole is different because of different effective masses and barrier heights, and, moreover, the HH and LH mixing makes the hole density distribution in the well quite different from the electron distribution especially for wider wells with stronger HH and LH mixing, the electron's and the hole's contribution would by no means cancel.

The allowed ($\Delta n = 0$) transition usually have larger oscillator strengths especially in narrower wells; on the other hand, since the difference between electron-phonon and hole-phonon Fröhlich interaction is larger for forbidden ($\Delta n \neq 0$) intrasubband scattering, which becomes effective only presuming that there are significant HH and LH mixing. Thus the allowed intrasubband channel dominates the F-process for narrower wells; while the intersubband and forbidden intrasubband channels dominate the F-scattering in wider wells. The numerical results show that the $CB2-LH1$ 2p-exciton mediated F scattering channel is the most important channel (for $n = 2$, i.e. the 1st A1 phonon mode) in spite of the well widths, which is not surprising in view of strong HH and LH mixing for LH1 and HH2 subbands near the zone-center in MQW$^{20,21}$. For the electron-hole pair mediated F-scattering, since the HH and LH mixing are sensitive to the parallel wave vector $k||$, the calculated Raman numerators are also $k||$-dependent, which can vary rapidly when two subbands are near their cross-over point. The calculated Fröhlich Raman numerators are comparable in magnitudes with that due to the DP scattering, so under the condition of resonant scattering, the F-process can be the dominant channel.

3.4 Phonon Parity Selection Rules

Since only one particle in the exciton can change its confinement quantum number, and from the optical transition the electron and the $j_o$ component of hole must have the same parity with respect to $z$-axis, the electrostatic potential in Eq.1 and the corresponding displacement function must be of even symmetry with the $z$-inversion. Therefore, even-mode (A1) LO phonons can be scattered via Fröhlich exciton-phonon interaction and odd-mode (B2) LO phonons are scattered via DP interaction and so do the TO modes associated with even displacement function of $z$.

3.5 Polarization Configurations

Since $j_o$ is conserved in the F process, it is only possible for $(++)$, $(--)$, or $(ss)$ polarized configuration; on the other hand, since $\Delta j_o = 2$ for $\alpha$-DP scattering, the band edge function changes from $X+iY$ (or $X-iY$) to $X-iY$ (or $X+iY$), it is only possible for $(+-)$ or $(-+)$ configuration in $zz$ backscattering. Thus, A1-phonons are dipole allowed for polarized configuration and B2-phonons for depolarized configuration. For the symmetry reason, TO-phonon induced scattering is hardly observed in the backscattering configurations, and becomes possible for 90° scattering.

4. DISCUSSIONS ON SOME SELECTED EXPERIMENTS

4.1 Asymmetry Between Incoming and Outgoing Resonance Peaks
In the resonant Raman profile, while the electron-hole pair mediated scattering provides the background, the peaks result mainly from the discrete exciton, therefore the resonant Raman scattering becomes an effective probe to the electronic structure in MQW's.\textsuperscript{6}

In Ref.6, Zucker et al has attributed the asymmetry between the incoming and outgoing resonances to the intersubband exciton- LO-phonon scattering. With our microscopic calculations, we have not found that their arguments are adequate. They neglected the contribution due to intrasubband scattering because they thought the intrasubband scattering could give no asymmetry to the resonant profile. In fact, the intrasubband and intersubband scattering might interfere in different ways, which makes the following statement not always true: Outgoing resonance dominates for transition to a higher-energy state and the incoming resonance peak is higher than the outgoing one in the case of transition to a lower-energy state. For example, our calculation indicates that the incoming resonance at 11H 1s-exciton (for 2nd A1 mode in a 102Å-well-width sample) dominates over outgoing resonance, whereas according to the above statement the outgoing resonance at the 11H 1s-exciton should always dominate.

4.2 Lineshapes of Raman Phonon Spectra

It is usually taken for granted that the phonon peaks of different n in the Raman spectra are different and the peak with smaller n has stronger strength because the normalisation constant is inversely proportional to n. Its correctness is only under the nonresonant conditions, but for the resonant scattering, the energy denominator has preference for some specific intermediate states which also select certain phonon mode according to the inner nodes of the intermediate envelope functions. We have evaluated Raman phonon spectra of \((GaAs)_{50}A(A/As)_{50}\) in \(z(xx)z\) and \(z(xy)z\) configuration for first eight phonon modes confined to GaAs layers. The calculated line shape of the phonon peak are shown to be sensitive to the incident light frequencies.

4.3 Selection Rules for Two-Phonon Raman Scattering

Recently, Alexandrou et al has measured triply resonant Raman scattering by selecting the well width such that the splitting of HH and LH subbands approximates the energy of two optical phonons.\textsuperscript{22} Based on our theory, the second-order Raman backscattering is allowed in the following cases.

(1). For depolarized scattering, the Raman-active modes are one A1 phonon plus one B2 phonon. The effective electron-phonon interaction mechanism is via one F-scattering plus one DP scattering.

(2). For polarized scattering, the Raman-active modes are either two A1 or two B2 phonons. The corresponding electron-phonon interaction mechanism is via either two F-scattering or two DP scattering.

In the experiment, where the incident photon is resonant with the LH1 subband, according to
our theory, the strongest channel is LH1-HH1-HH1 in the depolarized configuration, first via DP scattering (n=odd) then via F-scattering (n=even).

4.4 Effect of Applied Electric Field

When an electric field breaks the parity of the intermediate states, the phonon parity selection rule is no longer obeyed, but the the polarisation scheme mentioned above remains valid. In the presence of the field, the electron and hole move towards different direction, thus the intrasubband Fröhlich scattering with an antisymmetric potential due to normally forbidden phonon mode (B2mode) can become allowed, even stronger than that by allowed modes (A1 modes), because in this case the electron's and the hole's contribution to the F-scattering matrix elements will add up rather than mutually cancel.

5. CONCLUSIONS

Microscopic theory on Raman scattering in MQW's by optical phonons has been worked out systematically both for free electron-hole pairs and for discrete exciton states as intermediate states. The contributions by the electron-hole pairs show strong characteristic dependence on their parallel wave vector $k_{||}$. They are closely related to the subband structures of the quantum wells, in which heavy and light hole mixing plays an important role. Exciton mediated scattering bears a close relation to electron-hole pair contributions of small $k_{||}$, e.g. with respect to relative contributions from different subbands, and to variation with quantum well parameters, etc. However, a distinguishing feature of exciton-mediated scattering is the decisive role of the angular momentum state of the intermediate excitons; namely, s-state excitons predominate in the scattering. Unlike scattering in bulk materials, scattering through Fröhlich interaction in MQW's is no longer dipole forbidden, showing that it depends ultimately on barrier penetration and hole mixing effects. Based on the microscopic theory, several experiments are discussed and predicted.

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