Resonant Raman Scattering at the Critical Points of Semiconductors

K. P. Jain and Gayatri Choudhury
Physics Department, Indian Institute of Technology, Hauz Khas, New Delhi-29, India
(Received 18 September 1972)

We formulate a theory of the one-phonon resonant Raman scattering of light in semiconductors. Emphasis is placed on the scattering near the critical points. Resonance enhancement is found at the saddle points just as in the case of the M_0 edge. The effect of the electron-hole interaction on the scattering is discussed within the framework of the Slater–Koster interaction. An enhancement is predicted near the saddle points. The treatment is extended to include the effect of metastable excitons. Again an enhancement is predicted in addition to resonant scattering near the metastable exciton energies. It is suggested that more careful experiments are needed in the III-V and II-VI compounds to make contact with the theory.

I. INTRODUCTION

Resonant Raman scattering (RRS) is the enhancement of Raman scattering cross section when the frequency of the exciting radiation is near one of the allowed optical transitions of the medium. A theoretical description of RRS in semiconductors was first given by Loudon[1] for noninteracting Bloch electrons. He described light scattering at the M_0 edge with the assumption that virtual intermediate scattering states are free electron-hole pairs. Early work on CdS by Leite and Porto[2] showed an enhancement of Raman scattering (RS) cross section for laser energy slightly less than that of the direct gap. The observed enhancement was found to be more pronounced than predicted by Loudon's[1] theory.

A more complete theory was given by Ganguly and and Birman,[3] in which they took into account the interaction between electrons and holes. They considered hydrogenic excitons as the intermediate states in the scattering process. The experimental results of Leite and Porto[2] on CdS and ZnSe were found to be in agreement with the theoretical predictions of Ganguly and Birman.

Raman scattering measurements have also been made at the nonfundamental gaps, such as the E_1 saddle point in III-V compounds. Pinczuk and Burstein[4] report measurements on InSb. They observed a large scattering cross section with a He-Ne laser whose energy is near that of the E_1 edge in InSb.

This work was extended by Leite and Scott,[5] who measured scattering cross sections of InAs and InSb using argon-ion lasers. They showed that though there is an enhancement of scattering cross section in InAs at $E_1 \sim 2.5$ eV, no enhancement was observed in the case of InSb at $E_1+\Delta_1 \sim 2.5$ eV, the argon-ion lasers being operative at 2.50, 2.55, 2.60, and 2.65 eV. RS measurements were also made on GaAs and InP by Leite and Scott.[5] None of these materials were found to exhibit any significant dependence of RS cross section upon argon-laser frequency. In InAs overtone scattering was observed near the E_1 gap, while for GaAs no overtone scattering was observed. This is compatible with the fact that there is no interband gap in GaAs near the laser frequencies used. The absolute cross sections in GaAs were, in general, very large. Leite and Scott[5] plotted the scattering cross section in InAs as a function of laser frequency, and the resulting resonance curve was compared with that obtained in CdS and ZnSe.[2] The shapes of the curves were found to be quite different in the two cases. This shows that whereas Ganguly and Birman's theory predicts correct results at the M_0 edge, the behavior of the RS cross section at the saddle points cannot be described by their theory, since at a saddle point the exciton is no longer hydrogenic.

In this paper we formulate an approximate theory of resonant Raman scattering at saddle points. It is natural to emphasize the Van Hove critical-point dependence of the RS and this is done in Sec. II. Section III describes the RS amplitude at saddle points approximating the electron-hole (e-h) interaction by a Slater–Koster (SK) potential. The Coulomb nature of the e-h interaction at saddle points and its effect on the RS is discussed in Sec. IV. Concluding remarks are made in Sec. V.

II. RAMAN SCATTERING NEAR THE CRITICAL POINTS: NO ELECTRON-HOLE INTERACTION

We first calculate the RS amplitude at the M_0 edge in the absence of e-h interaction. The one-phonon Stokes RS amplitude $A(\omega)$ is given in perturbation theory by

$$A(\omega) \sim \int_0^{k_{\max}} d^3k \times \frac{1}{(\omega_g+\omega_0-\omega+\hbar k^2/2m)(\omega_g-\omega+\hbar k^2/2m)}, \qquad (1)$$

where ω and ω_0 are the energies of the incident photon and the phonon, respectively. The momentum dependence of the scattering matrix elements is neglected in Eq. (1). As a simple illustration and to establish the procedure for the saddle points, it is instructive to calculate the $A(\omega)$ appropriate to the M_0 edge. Assuming parabolic bands,

$$\omega_k = \omega_g + \hbar k^2/2m \ , \qquad (2)$$

k being the total wave vector and ω_g the band gap. Then, Eq. (1) becomes

$$A(\omega) \sim \int_0^{k_{\max}} \frac{d\omega_k}{(\omega_k+\omega_0-\omega)(\omega_k-\omega)} \int \frac{dS_k}{\nabla_k\omega_k} \ , \qquad (3)$$

where

$$\nabla_k\omega_k = (\hbar/m)k \ ,$$

and

$$dS_k = 4\pi k^2 \ . \qquad (4)$$

The integral

$$\int \frac{dS_k}{\nabla_k\omega_k}$$

is the interband density of states, which is $\sim(\omega_k - \omega_g)^{1/2}$ at the M_0 edge. Therefore Eq. (3) becomes

$$A(\omega) \sim \int_0^{k_{\max}} d\omega_k \frac{(\omega_k-\omega_g)^{1/2}}{(\omega_k-\omega)(\omega_k+\omega_0-\omega)} \ . \qquad (5)$$

Taking the upper limit of the above integral to be $|k_{\max}| = \infty$, we can evaluate it as a contour integral with the contour shown in Fig. 1. We find[1]

$$A(\omega) \sim (1/\omega_0)[(\omega_g+\omega_0-\omega)^{1/2} - (\omega_g-\omega)^{1/2}] \quad \text{if } \omega < \omega_g \qquad (6)$$

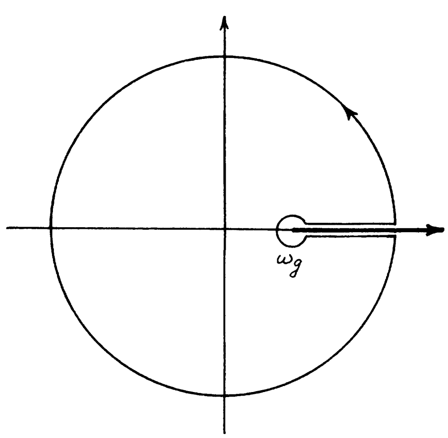

FIG. 1. Contour of integration used to calculate the integral in Eq. (5).

$$\sim (1/\omega_0)(\omega_g+\omega_0-\omega)^{1/2} \quad \text{if } \omega_g < \omega < \omega_g+\omega_0 \qquad (7)$$

$$\sim 0 \quad \text{if } \omega > \omega_g+\omega_0 \ . \qquad (8)$$

A constant-background density of states will only contribute a constant term to the Raman amplitude.

We will now calculate the RS amplitude at the M_1 saddle point. In this case we assume

$$\omega_k = \omega_g + (\hbar/2m)(k_\rho^2 - k_z^2) \ , \qquad (9)$$

where k_ρ is the wave vector in the basal plane, and k_z that along the z axis. Equation (9) has been put in the above form to take into account the signs of effective masses along the different principal directions. Again we can write down Eq. (3), i.e.,

$$A(\omega) \sim \int_0^{k_{\max}} \frac{d\omega_k}{(\omega_k+\omega_0-\omega)(\omega_k-\omega)} \int \frac{dS_k}{\nabla_k\omega_k} \ ,$$

where

$$dS_k = 2\pi(k_\rho^2 + k_z^2)^{1/2} dk_z$$

and

$$\nabla_k\omega_k = (\hbar/2m)(k_\rho^2+k_z^2)^{1/2} \ . \qquad (10)$$

For the present case, therefore, Eq. (3) becomes

$$A(\omega) \sim \int_0^{k_{\max}} \frac{d\omega_k}{(\omega_k+\omega_0-\omega)(\omega_k-\omega)} (k_{z\max} - k_{z\min}) \ . \qquad (11)$$

From Eq. (9) we find that

$$k_{z\min} = 0 \quad \text{if } \omega_k > \omega_g$$
$$= [(\omega_g-\omega_k)(2m/\hbar)]^{1/2} \quad \text{if } \omega_k < \omega_g \ . \qquad (12)$$

Since $k_{z\max}$ is a constant, the RS amplitude corresponding to it, i.e., the first term of Eq. (11), will be a slowly varying function of ω near ω_g which we call C. Therefore Eq. (11) becomes

$$A(\omega) \sim C - \int_0^{\omega_g} \frac{d\omega_k(\omega_g-\omega_k)^{1/2}}{(\omega_k+\omega_0-\omega)(\omega_k-\omega)} \ . \qquad (13)$$

The above integral can be evaluated using the contour shown in Fig. 2. The results obtained are

$$A(\omega) \sim C - (1/\omega_0)[(\omega-\omega_g)^{1/2} - (\omega-\omega_g-\omega_0)^{1/2}] \quad \text{if } \omega > \omega_g+\omega_0 \qquad (14)$$

$$\sim C - (1/\omega_0)(\omega-\omega_g)^{1/2} \quad \text{if } \omega_g < \omega < \omega_g+\omega_0 \qquad (15)$$

$$\sim C \quad \text{if } \omega < \omega_g \ . \qquad (16)$$

This determines Raman scattering for noninteracting electrons in the neighborhood of the M_1 critical point. The RS amplitude near the M_2 critical point can be calculated in a similar way. In the neighborhood of the M_2 saddle point, Eq. (9) is written

$$\omega_k = \omega_g - (\hbar/2m)(k_\rho^2 - k_z^2) \ , \qquad (17)$$

because the effective masses along the principal

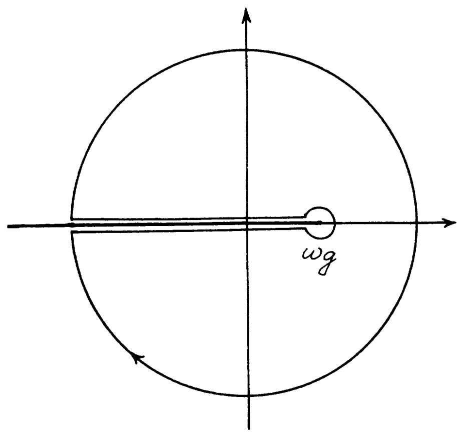

FIG. 2. Contour of integration used to calculate the integral in Eq. (13).

directions at M_2 have signs opposite to that of the corresponding effective masses at the M_1 saddle point. The Raman amplitude at the saddle point M_2 is given by Eq. (11), with

$$k_{z\,\min}=[(\omega_k-\omega_g)(2m/\hbar)]^{1/2} \quad \text{if } \omega_k>\omega_g \tag{18}$$

$$=0 \quad \text{if } \omega_k<\omega_g\,, \tag{19}$$

and $k_{z\,\max}$ is a constant. Then

$$A(\omega)\sim C-\int_{\omega_g}^{k_{\max}} \frac{d\omega_k(\omega_k-\omega_g)^{1/2}}{(\omega_k-\omega+\omega_0)(\omega_k-\omega)}\ . \tag{20}$$

Integrating, we get

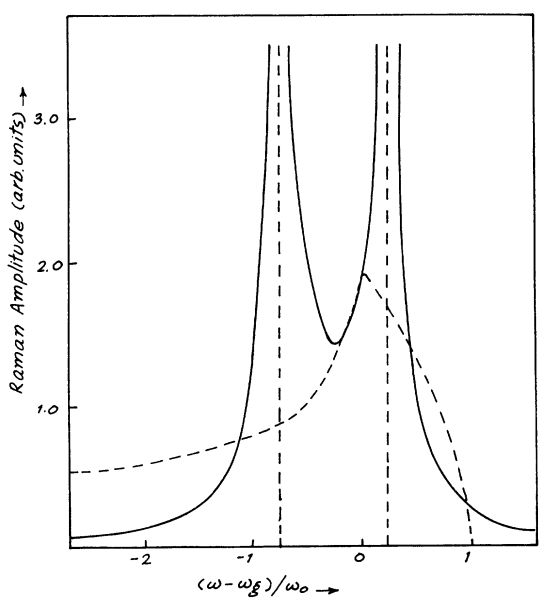

FIG. 3. First-order Stokes–Raman spectrum of a typical semiconductor (CdS) at the M_0 edge. The dashed line represents a fit to Eqs. (6)–(8) with $\omega_g=2.6$ eV and $\omega_0=37$ meV. The solid line represents Ganguly and Birman's result with $R'=28$ meV.

$$A(\omega)\sim C+(1/\omega_0)[(\omega_g-\omega)^{1/2}-(\omega_g-\omega+\omega_0)^{1/2}] \quad \text{if } \omega<\omega_g \tag{21}$$

$$\sim C-(1/\omega_0)(\omega_g-\omega+\omega_0)^{1/2} \quad \text{if } \omega_g<\omega<\omega_g+\omega_0 \tag{22}$$

$$\sim C \quad \text{if } \omega>\omega_g+\omega_0\ . \tag{23}$$

Equations (21)–(23) describe the RS for noninteracting electrons in the neighborhood of the M_2 saddle point. The behavior of the RS amplitude at the M_0, M_1, and M_2 critical points for noninteracting electrons is shown in Figs. 3 and 4.

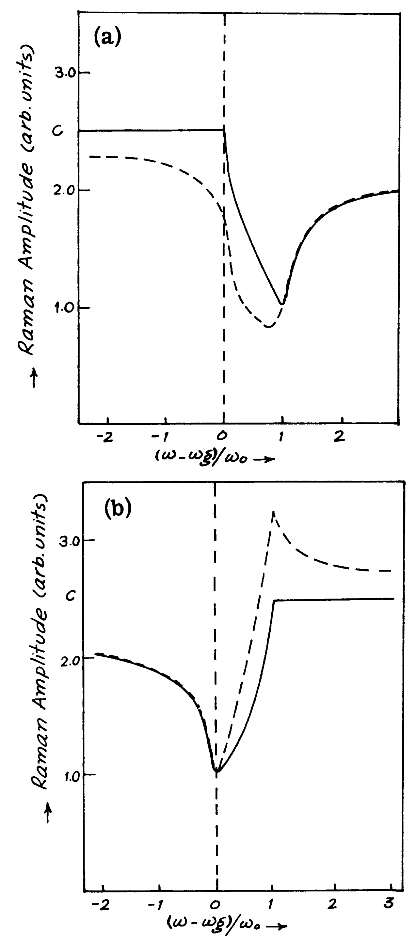

FIG. 4. (a) First-order Stokes–Raman spectrum of a typical semiconductor at the M_1 edge. The solid line is a fit to Eqs. (14)–(16) for typical values in II-VI semiconductors. The dashed line is obtained by evaluating Eqs. (36)–(38), taking $|g|=0.12$ eV and $K=1$. (b) First-order Stokes–Raman spectrum of a typical semiconductor at the M_2 edge. The solid line corresponds to the case of noninteracting electrons. The dashed line is obtained by considering SK interaction between an e-h pair. The value of constant C has been chosen arbitrarily in both the cases.

III. EXCITON EFFECTS: SLATER-KOSTER INTERACTION

So far the interaction between electron and hole has been neglected; i.e., we have considered free e-h pairs as the intermediate scattering states. Ganguly and Birman[3] extended the calculation of the RS amplitude to include the effect of hydrogenic excitons at the M_0 edge. Their theory is inapplicable to RRS near the M_1 edge, since Coulomb effects at the saddle points do not result in hydrogenic excitons.

Several models have been given for the e-h interaction at the M_1 edge.[6] The common feature of these models is the truncation of the interaction beyond a certain value of the e-h separation r. The simplest of these is the SK contact interaction potential $V(r)=\delta(r)g$, which is zero except when the electron and hole are in the same unit cell. This model has been used to discuss the metamorphism of the critical points due to e-h interaction discussed by Velicky and Sak[7] and Toyozawa.[8] Further, it has been used to discuss Coulomb effects on electroreflectance line shapes by Rowe and Aspnes.[9] In this case the result is model independent, since the exciton binding energies are of the same order of magnitude as the phonon broadening. Therefore it is meaningful to discuss RRS at saddle points within the framework of this model.

The SK potential in the k representation is given by

$$\langle k|\,V|\,k'\rangle = gN^{-1}\delta_{kk'} \tag{24}$$

for all states belonging to a given set of valence and conduction bands. N is the number of unit cells per unit volume and g is a constant which gives the strength of the interaction.

The RS amplitude at a critical point can be written

$$A(\omega)\sim\int d^3k \times\frac{|\phi^s(0)|^2}{(\omega_g-\omega+\hbar k^2/2m)(\omega_g+\omega_0-\omega+\hbar k^2/2m)}\,. \tag{25}$$

Here $\phi^s(0)$ is the envelope function of the exciton. From Velicky and Sak[7] we have

$$|\phi^s(0)|^2 = 1/|1+gF(\omega)|^2\,, \tag{26}$$

where

$$F(\omega) = -N^{-1}\int_{-\infty}^{\infty}\frac{d\omega'\,N_d(\omega')}{\omega-\omega'+i\eta}\;, \tag{27}$$

$N_d(\omega')$ being the joint density of states. For $gF(\omega)\ll 1$,

$$1/|1+gF(\omega)|^2 = 1-2g\,\mathrm{Re}F(\omega)\,. \tag{28}$$

For an attractive e-h interaction, Eq. (25) becomes

$$A(\omega)\sim\int d^3k\,\frac{1}{(\omega_k-\omega+\omega_0)(\omega_k-\omega)} \times[1+2|g|\,\mathrm{Re}F(\omega_k)]\,, \tag{29}$$

where real part of $F(\omega)$ is the Hilbert transform of $N_d(\omega)$:

$$\mathrm{Re}F(\omega)=N^{-1}\mathcal{P}\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega}\,N_d(\omega')\,. \tag{30}$$

The RS amplitude at the saddle points can be calculated by rewriting Eq. (29) with the help of Eq. (11):

$$A(\omega)\sim\int_0^{\infty}\frac{d\omega_k\,(k_{z\,\max}-k_{z\,\min})}{(\omega_k-\omega+\omega_0)(\omega_k-\omega)} \times[1+2|g|\,\mathrm{Re}F(\omega_k)]\,. \tag{31}$$

Simple integration of Eq. (30) gives

$$\begin{aligned}\mathrm{Re}F(\omega) &\sim -\pi(\omega-\omega_g)^{1/2} && \text{if } \omega>\omega_g\\ &\sim 0 && \text{if } \omega<\omega_g\end{aligned} \tag{32}$$

for $\mathrm{Re}F(\omega)$ at the M_1 saddle point, and

$$\begin{aligned}\mathrm{Re}F(\omega) &\sim \pi(\omega_g-\omega)^{1/2} && \text{if } \omega<\omega_g\\ &\sim 0 && \text{if } \omega>\omega_g\,.\end{aligned} \tag{33}$$

at the M_2 saddle point. Combining Eqs. (31) and (32) one gets

$$A(\omega)\sim\int_0^{\omega_g}\frac{d\omega_k}{(\omega_k+\omega_0-\omega)(\omega_k-\omega)}[k_{z\,\max}-(\omega_g-\omega_k)^{1/2}] +\int_{\omega_g}^{\infty}\frac{d\omega_k\,k_{z\,\max}}{(\omega_k+\omega_0-\omega)(\omega_k-\omega)} \times[1-2\pi|g|(\omega_k-\omega_g)^{1/2}] \tag{34}$$

for the M_1 point. The values of $k_{z\,\min}$ have been taken from Eq. (12). We have already stated in Sec. II that the integral

$$\int_0^{k_{\max}}\frac{d\omega_k}{(\omega_k+\omega_0-\omega)(\omega_k-\omega)}\,k_{z\,\max}\sim C\,. \tag{35}$$

The integrals on the right-hand side of Eq. (34) are evaluated using suitable contours as before. We arrive at the following results for an M_1 saddle point:

$$A(\omega)\sim C+\frac{2\pi|g|K}{\omega_0}[(\omega_g-\omega)^{1/2}-(\omega_g-\omega+\omega_0)^{1/2}] \qquad \text{if } \omega<\omega_g \tag{36}$$

$$\sim C-\frac{1}{\omega_0}(\omega-\omega_g)^{1/2}-\frac{2\pi|g|K}{\omega_0}(\omega_g+\omega_0-\omega)^{1/2} \qquad \text{if } \omega_g<\omega<\omega_g+\omega_0 \tag{37}$$

$$\sim C-(1/\omega_0)[(\omega-\omega_g)^{1/2}-(\omega-\omega_g-\omega_0)^{1/2}] \qquad \text{if } \omega>\omega_g+\omega_0\,, \tag{38}$$

where we have replaced $k_{z\,max}$ by K. Similarly at the M_2 saddle point, we obtain

$$A(\omega) \sim C + (1/\omega_0)[(\omega_g - \omega)^{1/2} - (\omega_g - \omega + \omega_0)^{1/2}] \quad \text{if } \omega < \omega_g \tag{39}$$

$$\sim C + \frac{2\pi|g|K}{\omega_0}(\omega - \omega_g)^{1/2} - \frac{1}{\omega_0}(\omega_g + \omega_0 - \omega)^{1/2} \quad \text{if } \omega_g < \omega < \omega_g + \omega_0 \tag{40}$$

$$\sim C + \frac{2\pi|g|K}{\omega_0}[(\omega - \omega_g)^{1/2} - (\omega - \omega_g - \omega_0)^{1/2}] \quad \text{if } \omega > \omega_g + \omega_0 \,. \tag{41}$$

The results for the M_1 and M_2 critical points are compared with the corresponding ones for the noninteracting electron in Figs. 4(a) and 4(b). By way of comparison, Fig. 3 illustrates the difference in the Raman amplitudes near the M_0 edge for the noninteracting electrons and hydrogenic exciton models.

IV. EXCITON EFFECTS: COULOMB INTERACTION

Coulomb interaction between an e-h pair at saddle points leads to resonances or metastable excitons which give rise to characteristic line shapes in the optical spectra of semiconductors.[10] Metastable excitons are different in character from the hydrogenic ones. The theory of the metastable excitons is made complicated by the nature of the energy surfaces and it is only recently that a quantitative theory was given.[7,11]

The envelope function for Coulomb effects at the M_1 edge is

$$|\phi_n^s(0)|^2 = \frac{16 m_\perp^3}{\pi\epsilon^2(2n-1)^3} \,, \tag{42}$$

for the resonant states, where $m_\perp$ is the transverse mass, and

$$|\phi(0)|^2 = e^{-\gamma}/\cosh\gamma \tag{43}$$

for the continuum states, where

$$\gamma(\omega) = -\frac{\pi|W_1(0)|^{1/2}}{2(\omega - \omega_g)^{1/2}} \tag{44}$$

and

$$W_n(0) = -\frac{2m_\perp}{\epsilon_0^2(2n-1)^2} \,, \quad n = 0, 1, 2, \ldots \,. \tag{45}$$

The RS amplitude, Eq. (25), becomes

$$A(\omega) \sim \sum_n \frac{16 m_\perp^3}{\pi\epsilon^2(2n-1)^3} \times \frac{1}{[\omega_g - W_n(0) - \omega][\omega_g + \omega_0 - W_n(0) - \omega]} + \int_{\omega_g}^{\infty} \frac{d^3k}{(\omega_k + \omega_0 - \omega)(\omega_k - \omega)} \frac{e^{-\gamma}}{\cosh\gamma} \,. \tag{46}$$

The integral in Eq. (46) is simply evaluated as

$$\left\{1 + \exp\left[-\left(\frac{\pi^2 W_1}{\omega_g - \omega}\right)^{1/2}\right]\right\}^{-1} - \left\{1 + \exp\left[-\left(\frac{\pi^2 W_1}{\omega_g + \omega_0 - \omega}\right)^{1/2}\right]\right\}^{-1} \,. \tag{47}$$

When the energy of the incident photon is near one of the metastable resonant energies $\omega_g - W_n(0)$, the Raman amplitude becomes

$$A(\omega) \sim \sum_n \frac{16 m_\perp^3}{\pi\epsilon^2(2n-1)^3} \times \frac{1}{[\omega_g - W_n(0) - \omega][\omega_g + \omega_0 - W_n(0) - \omega]} \,. \tag{48}$$

The result is analogous to that obtained by Ganguly and Birman[3] for the hydrogenic excitons and has the same analytic structure; i.e., the amplitude diverges at the resonance. For photon energies far away from the metastable resonant energies, the Raman amplitude is given by Eq. (47).

V. DISCUSSION AND CONCLUDING REMARKS

The Raman scattering amplitude has been calculated in the vicinity of the various critical points and the results are plotted in Figs. 3 and 4.

As noted elsewhere, the Raman amplitude is enhanced when the energy of the incident light approaches that of the M_0 edge. Hydrogenic excitons are incorporated into the theory[3] and again one finds resonance enhancement near the discrete (exciton) energies and near the continuum (M_0 edge).

A similar analysis can be given for the M_1 edge. For noninteracting electrons the results are given by Eqs. (14)–(16), and are plotted in Fig. 4(a). In this case one gets an enhancement of the scattering as the photon energy approaches $\omega_g + \omega_0$ from the high-energy side. A similar enhancement is expected as one approaches the M_1 edge from the low-energy side. Typical resonant structure would be found between ω_g and $\omega_g + \omega_0$. The situation for the M_2 edge is similar and is given in Fig. 4(b).

Coulomb effects at the saddle points complicate the situation considerably. Assuming a SK model for the e-h interaction, the $A(\omega)$ is given by Eqs. (36)–(38) for the M_1 edge. The effect of this is to reduce the enhancement near the edge compared to the noninteracting case [see Fig. 4(a)]. This is analogous to the smearing out of the singularity in the real part of the dielectric function $\epsilon_1(\omega)$ near the M_1 edge due to e-h interaction.[8] Similarly, the SK model near the M_2 edge sharpens the structure [see Fig. 4(b)].

A more realistic treatment of the e-h interaction leads to the existence of metastable (hyperbolic) exciton resonances near the M_1 edge. Typical resonant structure associated with these resonances appears in the RS amplitude, Eq. (47). This is analogous to the resonant scattering owing to hydrogenic excitons near the M_0 edge. In addition to resonant scattering, scattering due to the continuum states takes place near the M_1 edge. The problem is similar to that of the dual relationship between the local and band aspects, which results in the metamorphosis of the critical points.[7,8] The precise extent to which the singularity at the M_1 edge would be smeared out would depend upon the detailed study of the interference effect between the resonant and continuum states. The resonant states would be modified to include an antiresonance, whereas the Van Hove singularity would be modified suitably. The qualitative trends are, however, clear: the Raman amplitude at the M_1 and M_2 edges would be smeared out and sharpened, respectively. Such effects may be masked by broadening due to phonons, defects, and electron correlations.

The resonance enhancement in the RS due to discrete and continuum at the M_0 edge has been studied experimentally in detail, and the agreement between theory and experiment is good. The situation for the M_1 edge is less clear owing to the paucity of experimental data. This can be remedied only by more careful experiments near the M_1 edge in III-V compounds.

The structure due to the metastable excitons in the optical spectra of III-V compounds is weak, and typically the binding energies are of the order of magnitude of phonon linewidths. Consequently their effect on the RS at the M_1 edge is likely to be small. Optical spectra of some II-VI compounds, e.g., CdTe, show prominent peaks due to metastable excitons with large binding energies. RS experiments at these energies would determine the effect of these resonant states on the scattering process.

The above remarks hold provided the momentum dependence of the scattering matrix elements is neglected in Eq. (1). This approximation is valid if the dominant electron-phonon coupling is of the deformation-potential type.[12] It has been found that there is a breakdown of dipole selection rules in RRS[13] when the energy of the incident light is near that of the 1s hydrogenic exciton in CdS. This is due to interactions which are linear in the excitation momentum q, so that the scattering amplitude is proportional to qa_0, where a_0 is the radius of the exciton. For CdS the radius of the 1s Wannier exciton is 28 Å, i.e., $qa_0 = 0.15$. The forbidden scattering which takes place through momentum-dependent Fröhlich interaction, shows rapid enhancement for photon energies near those of large-radius Wannier excitons and result in Raman cross sections comparable to those for allowed scattering. In this case, Eq. (1) must be modified to include the momentum dependence of the matrix elements. Away from resonance, forbidden scattering decreases rapidly and become small compared to allowed scattering.

The situation for metastable excitons is similar. For III-V compounds the exciton radius is large, and so one might expect a large q-dependent forbidden scattering. In actual fact, owing to the small oscillator strength of the exciton, continuum scattering would predominate.

The situation for II-VI compounds is quite different. Here the metastable excitons have large oscillator strengths and radii. For instance in CdTe,[14] the exciton radius is 25 Å, which is comparable to that of the 1s hydrogenic exciton in CdS. Therefore, in this case a large q-dependent forbidden resonant scattering is expected.

ACKNOWLEDGMENTS

This work was begun when one of the authors (K. P. J.) was at the International Center for Theoretical Physics, Trieste, Italy. He wishes to express his thanks to Professor A. Salam and Professor P. Budini for their kind hospitality. Thanks are also due to Professor S. Lundquist for his interest in the work.

---

[1]R. Loudon, Proc. Phys. Soc. Lond. **82**, 393 (1963).

[2]R. C. C. Leite and S. P. S. Porto, Phys. Rev. Lett. **17**, 10 (1966).

[3]A. K. Ganguly and J. L. Birman, Phys. Rev. **162**, 806 (1967).

[4]A. Pinczuk and E. Burstein, Phys. Rev. Lett. **21**, 1073 (1968).

[5]R. C. C. Leite and J. F. Scott, Phys. Rev. Lett. **22**, 130 (1969).

[6]Y. Toyozawa, M. Inoue, T. Inui, M. Okazaki, and E. Hanamura, J. Phys. Soc. Jap. Suppl. **21**, 133 (1967); J. Hermanson, Phys. Rev. **166**, 893 (1968).

[7]B. Velicky and J. Sak, Phys. Status Solidi **16**, 147 (1966).

[8]Y. Toyozawa *et al.*, J. Phys. Soc. Jap. 22, 1337 (1967).

[9]J. E. Rowe and D. E. Aspnes, Phys. Rev. Lett. **25**, 162 (1970).

[10]J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vol. 18, p. 125; K. P. Jain, Phys. Rev. **139**, A544 (1965).

[11]E. O. Kane, Phys. Rev. **180**, 852 (1969).

[12]R. M. Martin, Phys. Rev. B **4**, 3676 (1971); R. M. Martin, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 25.

[13]R. M. Martin and T. C. Damen, Phys. Rev. Lett. **26**, 86 (1971).

[14]M. Balkanski and Y. Petroff, Phys. Rev. B **3**, 3299 (1971).