Resonant Raman scattering in GaP: Excitonic and interference effects near the E_0 and $E_0+\Delta_0$ gaps

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We report on the Raman scattering by LO phonons resonant near the E_0 and $E_0+\Delta_0$ gaps of GaP. Dipole-allowed and dipole-forbidden Raman scattering by LO phonons and their interference are observed, together with scattering by two-LO phonons. The dominant features in the resonant profiles arise from the E_0 gap. They cannot be interpreted with uncorrelated electron-hole pairs. Martin's calculations for Coulomb-correlated pairs explain qualitatively the resonance enhancement of one-LO-phonon scattering below the E_0 gap, whereas a simple Lorentzian oscillator model accounts for the observed features and the signs in the interference profiles above E_0.

I. INTRODUCTION

The resonance of first- and second-order Raman scattering near the E_0 and $E_0+\Delta_0$ gaps of GaP was investigated by Weinstein and Cardona[1] using the discrete lines of an Ar^+ and a He-Cd laser and temperature tuning of the energy gap. Their work was aimed at the observation of TO dipole-allowed, LO dipole-forbidden, TO + LO, and two-LO-phonon scattering and their resonance. The experimental data were explained as resonances at uncorrelated electron-hole critical points. More complete results for the one-phonon scattering were obtained by Bell *et al.*[2] using a pulsed-dye laser.

Since then, a lot of progress has been made in our understanding of the resonance by LO phonons. Near the spin-orbit-split direct gap $E_0+\Delta_0$ of high-purity GaAs,[3–5] InP,[6] and GaSb,[7] the dipole-forbidden scattering by LO phonons arising from the **q**-dependent intraband electron-phonon Fröhlich interaction (FI), has been shown to interfere with the dipole-allowed deformation potential (DP) and the electro-optic (EO) scattering. In addition, elastic scattering by ionized impurities enhances the forbidden scattering.[8] This process is incoherent with the deformation potential and **q**-dependent (FI) scattering since wave-vector conservation is relaxed in this process. Good agreement between theory and experiment was found assuming free electron-hole pairs and accounting for Coulomb-correlation effects in an *ad hoc* way by enhancing numerical prefactors.

Below the E_0 gap of GaAs no significant interference effects were observed.[9] The interpretation of the resonance of the allowed and forbidden scattering required Coulomb interaction between excited electron-hole pairs. unfortunately, measurements immediately above E_0 in GaAs and other direct-gap semiconductors are hampered by strong luminescence.

For indirect-gap semiconductors hardly any luminescence is seen at the lowest direct gap (E_0). Thus detailed Raman measurements become possible around E_0 at the expense of a lifetime broadening of this critical point. Such measurements are presented here for GaP.

II. EXPERIMENT

The samples (thickness 500 μm) were cut from an undoped single crystal ($n\cong 10^{15}$ cm^{-3}). Backscattering in the four different configurations (I–IV) on a (001) face, as described in Refs. 4 and 5, was used to measure the dipole-allowed and dipole-forbidden scattering by LO phonons as well as their interference. Here x, y, z, x', and y' denote the [100], [010], [001], [110], and [$\bar{1}$10] directions, respectively. The [110] and [$\bar{1}$10] directions were determined by inspection of the etch pattern produced by the etchant $2HNO_3(70\%):1HCl(36\%)$.[10]

In order to obtain absolute Raman scattering efficiencies we used the sample substitution method[11] with BaF_2 as a reference [$|a|=0.93$ Å^2, $\partial S/\partial\Omega=5.5\times10^{-8}$ sr^{-1} cm^{-1} at $\hbar\omega_L=2.71$ eV (Ref. 12)]. The corrections for absorption, refractive index, and reflectivity were carried out with Eq. (10) of Ref. 9 using optical data for BaF_2 from Ref. 13. For GaP the absorption corrections around E_0 are more delicate. Absorption data at 25 K from Dean *et al.*[14] were shifted and the exciton peaks broadened so as to simulate data at 100 K. The additional optical constants were taken from ellipsometric data.[15]

The Raman measurements were performed for laser photons of energies between 2.79 and 3.05 eV. cw dye lasers with Stilbene 1 and Stilbene 3 (Lambda Physik, Göttingen) were pumped with 3 W of all uv lines of an Ar^+ laser. The power incident on the sample was between 2 and 30 mW. Above $\hbar\omega_L=2.79$ eV the absorption constant of GaP is larger than 1000 cm^{-1} and the penetration depth of the light becomes less than the thickness of the sample (500 μm).

III. RESULTS AND DISCUSSION

Figure 1 displays the resonance of the dipole-allowed (DP + EO, crosses) and dipole-forbidden (FI, triangles) Raman scattering by LO phonons below and slightly above the E_0 gap. The solid lines are drawn as a guide to the eye. The energy scale is chosen in units of the 1*s*-exciton binding energy [11 meV (Ref. 16)] in order to

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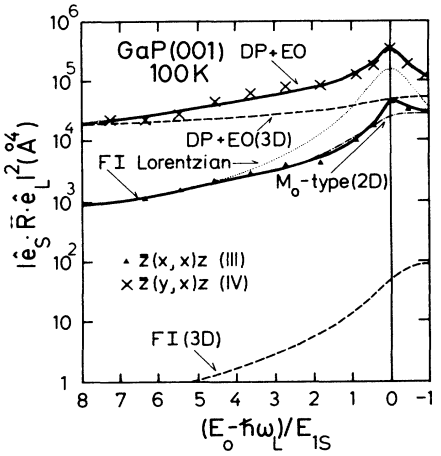

FIG. 1. Resonance of the dipole-allowed (DP + EO) and dipole-forbidden (FI) scattering below the E_0 gap of GaP. The solid lines are drawn through experimental points as a guide to the eye. The dashed lines correspond to calculations which assume free electron-hole pairs and three-dimensional bands (3D), the dotted and dot-dashed lines correspond to a Lorentzian and a logarithmic 2D minimum line shape, respectively. The unit of energy E_{1s} is 11 meV.

compare the data with the enhancement factors calculated by Martin for CdS (Ref. 17) as was done in Ref. 9 for GaAs.

The dashed curves are calculated with Eq. (1) (DP + EO) and Eqs. (6) and (7) (FI) of Ref. 9 assuming uncorrelated electron-hole pairs. The strength of the FI (3D) scattering was estimated from material parameters appropriate to GaP (Table I). The prefactors of the DP + EO (3D) scattering A_1 and A_2 were determined to be 6 Å^2 and 20 Å^2 from the observed behavior below 2.80 and above 3.0 eV (see Fig. 2). Choosing $A_3=0$ all additional contributions to the Raman polarizability were lumped into the real parameter A_2. With Eqs. (20) and (21) of Ref. 5 we can relate A_1 and A_2 to the optical deformation potentials d_0 and $d^5_{3,0}+(1/2\sqrt{2})d^5_{1,0}$. We obtain $C_0'' d_0=135$ eV and $d^5_{3,0}+(1/2\sqrt{2})d^5_{1,0}=73.6$ eV.[11] The last value is larger than theoretical estimates of the deformation potentials,[19] probably because of having neglected A_3. On the other hand, with C_0'' from 3.8 to 5.5, as determined from the birefringence induced by a [111] stress,[20] we obtain values of d_0 from 35 to 24 eV, in rather good agreement with theoretical values (38 eV from tight-binding, 29 eV from empirical pseudopotential,[21] and 24 eV from the linear muffin-tin orbital calculations[22]). Lawaetz,[23] however, estimated a higher value ($d_0=47$ eV) from the width of the E_0 and $E_0+\Delta_0$ gaps.

TABLE I. Material parameters appropriate to GaP.

$E_0=2.860\pm0.005$ eV[a]	$m_e=0.12m$[c,d]
$E_0+\Delta_0=2.940\pm0.005$ eV[a]	$m_{s.o.}=0.24m$[c,d]
$\eta^+=6$ meV[b]	$m_{lh}=0.16m$[c,d]
$\eta^-=12$ meV[b]	$m_{hh}=0.79m$[c,d]
$E_1=3.8$ eV	$P^2/m=10.5$ eV[c,d]
$E_1+\Delta_1=3.9$ eV	$C_F=3\times10^{-5}$ eV cm$^{1/2}$[d]
$\hbar\Omega_{LO}=50$ meV	

[a]From the position of the resonance.
[b]Reference 16.
[c]Reference 18 and **k**·**p** expressions.
[d]For definition see Ref. 9.

The agreement between the 3D calculations for allowed scattering using uncorrelated pairs is poor at resonance (Fig. 1) while it represents well the observed intensities farther away from the E_0 gap. The dipole-allowed scattering is enhanced between E_0-8E_{1s} and E_0 by a factor of 17, the dipole-forbidden one by a factor of 47. We can compare the observations with a calculation of Martin[17] using as intermediate states Coulomb-correlated electron-hole pairs. These calculations were performed for CdS; the different binding and excitation energies can be rescaled to those for GaP as done in Ref. 9 for GaAs. The excitonic contribution to the imaginary part of the dielectric function ϵ_i should thus be for GaP 0.28 times that of CdS. From Figs. 2 and 3 of Ref. 17 we obtain the following enhancement factors for the excitonic contributions to resonant Raman scattering in GaP: 19 for dipole-allowed deformation potentials and 8000 for dipole-forbidden Fröhlich-induced scattering at $1.4E_{1s}$ (15 meV) below E_0. From Fig. 1 we read the values of 3 for dipole-allowed and 700 for dipole-forbidden Raman scattering by LO phonons, smaller than the calculated ones. However, Martin's theory does not include the finite broadening of the E_0 gap which is particularly large for indirect-gap semiconductors. On the other hand, the experiment reflects well the theoretical prediction that the FI-induced scattering should be enhanced 5–10 times more than the allowed scattering.[24]

In Ref. 9 the effects of the discrete $n=1$ exciton state and the exciton continuum were simulated by Lorentzian [Eq. (14) of Ref. 9] and logarithmic [two-dimensional minimum, Eq. (13) of Ref. 9] line shapes, respectively. Figure 1 compares such curves calculated for $\eta=6$ meV (Ref. 16) with the experiments. Below the E_0 gap the agreement seems to be better for the 2D line shape in GaP, while a better agreement was found in GaAs for the Lorentzian line shape. In both materials the com-

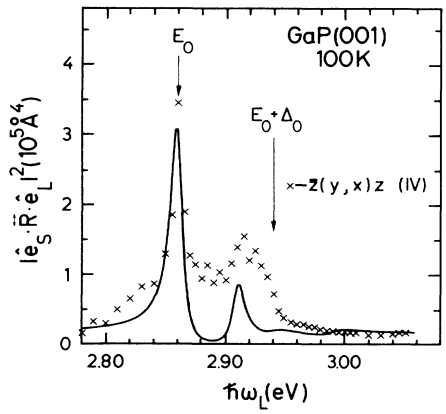

FIG. 2. Resonance of the dipole-allowed scattering near E_0 and $E_0+\Delta_0$ (crosses). The solid line represents calculations with Eqs. (1)–(4) which assume Lorentzian oscillators and two-band (2B) and three-band (3B) electron-phonon coupling.

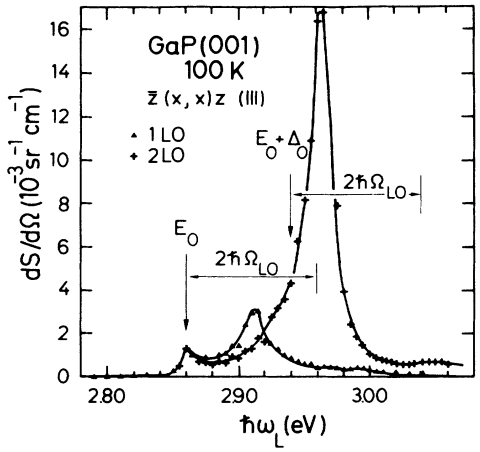

FIG. 3. Measured resonance profiles of the dipole-forbidden scattering by one-LO and two-LO phonons. The lines are a guide to the eye.

parison indicates that the ideal curve should be an admixture of both. The less pronounced Lorentzian behavior of the resonance enhancement below E_0 with respect to GaAs, in spite of the larger exciton binding energy (11 versus 4.2 meV), must be interpreted as due to the larger broadening (6 versus 2 meV).

Figure 2 shows the experimental data (crosses) for allowed scattering by LO phonons across the E_0 and $E_0+\Delta_0$ gaps. An incoming and an outgoing resonance is seen at E_0, the former being stronger than the latter. This fact cannot be explained by a theory assuming free electron-hole pairs as can be seen from the calculation of the F and G functions in Ref. 11 (pp. 114 and 115). The observation must be attributed to the Coulomb correlation of electron-hole pairs.

Before entering into a simple model calculation of the observed features, which is represented by the solid line of Fig. 2, we discuss the experimental data on the resonance of dipole-forbidden Raman scattering by one-LO and two-LO phonons. Figure 3 depicts the experimental results (the lines are drawn as a guide to the eye). Contrary to the resonance near $E_0+\Delta_0$ in other III-V compounds[5–7,25] the two-LO phonon scattering shows an *incoming* and an *outgoing* resonance. This fact cannot be represented by a 3D theory assuming free electron-hole pairs and light- and heavy-hole contributions.[6,25,26] The absence of the intermediate resonance $\hbar\omega_L = E_0 + \hbar\Omega_{LO}$ is in qualitative agreement with predictions from calculations which assume a strong Coulomb interaction between electrons and holes in the intermediate states for II-VI compounds.[27] In addition, a "fit" of the width of the two-LO outgoing-resonance profile would require unreasonably small broadenings, lower than 1 meV. The maximum scattering efficiency for two-LO-phonon scattering amounts to $1.5\times10^{-2}\ sr^{-1}\,cm^{-1}$. It is about 10^3 times stronger than that reported for GaAs and InP at $E_0+\Delta_0$. On the high-energy side of the two-LO-resonance curve we recognize a feature nearly 2 orders of magnitude weaker which can be attributed to the $E_0+\Delta_0$ resonance. Weak structures probably due to $E_0+\Delta_0$ are also seen for the one-LO profile at the tail of the outgoing resonance near the E_0 gap (Figs. 2 and 4).

The forbidden one-LO resonance near E_0 appears stronger for the outgoing resonance than for the incoming one (Fig. 3). This fact can be related to an impurity-induced contribution to the dipole-forbidden scattering.[4,6] In bulk GaSb only 30% of the dipole-forbidden scattering near the $E_0+\Delta_0$ was of intrinsic origin.[6]

The upper part (a) of Fig. 4 shows resonant interference profiles near the E_0 gap of GaP obtained in three scattering configurations ($\hat{e}_S \| \hat{e}_L$).[4,5] The interference effects are dominated by the E_0 structure. Below the E_0 gap the interference between dipole-allowed and dipole-forbidden scattering is weak: the Raman tensor for DP scattering is real, while that of the FI-induced scattering is purely imaginary. This observation agrees with that in GaAs where no interferences below E_0 were seen.[9] In GaAs the absence of interference below E_0 should be more pronounced since this gap is three times sharper than in GaP. At the E_0 gap the $\bar{z}(x',x')z$(I) and $\bar{z}(y',y')z$(II) configurations resonate differently. The outgoing resonance seems to be broader than the incoming one. The observed sign in the interference is the same at E_0 as at $E_0+\Delta_0$. The three-band contributions of DP

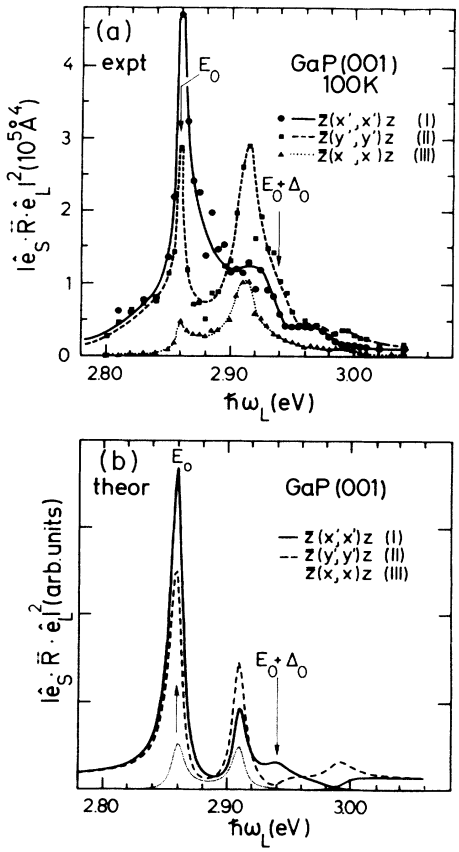

FIG. 4. Interference profile for the Raman scattering by LO phonons obtained with $\hat{e}_S \| \hat{e}_L$ in GaP. (a) Experimental points and lines drawn as a guide to the eye. (b) Result of calculation with the simple oscillator model as described in the text.

scattering are dominant near $E_0+\Delta_0$ where the observed sign of the interference is the same as in GaAs, InP, and GaSb.[3–7] If three-band terms were dominant for DP scattering at E_0, the sign of the interference should reverse from E_0 to $E_0+\Delta_0$ because of the reversing energy denominators. We thus conclude that the two-band terms are dominant at E_0 and that they have the same sign as the three-band contributions to the dipole-allowed scattering at the $E_0+\Delta_0$ gap.

In order to circumvent the lack of a realistic theory to describe the resonant scattering by LO phonons below and above the E_0 gap, including Coulomb correlation, we used a simple model based on Lorentzian oscillators. The relation between the two- and three-band terms in Raman scattering and the electronic contribution to the electronic susceptibility should be given by[28]

$$\overleftrightarrow{\chi}^{2B}(\hbar\omega_L)\cong(H_{eL})_{2B}\frac{\overleftrightarrow{\chi}^{E_0}(\hbar\omega_L)-\overleftrightarrow{\chi}^{E_0}(\hbar\omega_S)}{\hbar\Omega_{LO}}\ , \tag{1}$$

$$\overleftrightarrow{\chi}^{3B}(\hbar\omega_L)\cong(H_{eL})_{3B}\frac{\overleftrightarrow{\chi}^{E_0}(\hbar\omega_L)+\overleftrightarrow{\chi}^{E_0}(\hbar\omega_S)-\overleftrightarrow{\chi}^{E_0+\Delta_0}(\hbar\omega_L)-\overleftrightarrow{\chi}^{E_0+\Delta_0}(\hbar\omega_S)}{2\Delta_0}\ , \tag{2}$$

with $\hbar\omega_S=\hbar\omega_L-\hbar\Omega_{LO}$ and $(H_{eL})_{2B}$ and $(H_{eL})_{3B}$ the corresponding two- and three-band matrix elements in the electron-phonon interaction.

We assume the electronic susceptibilities to be Lorentzian, corresponding to the $n=1$ discrete exciton states:

$$\overleftrightarrow{\chi}^{E_0}\propto\frac{2}{\hbar\omega_L-E_0+i\eta^+}\ , \tag{3}$$

and

$$\overleftrightarrow{\chi}^{E_0+\Delta_0}\propto\frac{1}{\hbar\omega_L-E_0-\Delta_0+i\eta^-}\ . \tag{4}$$

$\eta^{\pm}$ are the broadenings of the corresponding gaps [$\eta^+=6$ meV, $\eta^-=12$ meV (Ref. 16)]. The factor of 2 in Eq. (3) accounts for the degeneracy of the Γ_8 valence band.

For DP scattering, 2B and 3B terms of Eqs. (1) and (2) are taken, whereas for FI-induced scattering only 2B terms similar to those of Eq. (1) are considered at the E_0 and $E_0+\Delta_0$ gap.

Figure 4(b) (lower part) and the solid line in Fig. 2 represent a calculation with the parameters of GaP (Table I) and appropriate prefactors. A real constant was added to a_{DP} in order to account for higher transitions and the observed scattering intensity below the E_0 gap. The relative signs of the Raman polarizability a_{DP} and a_{FI} at E_0 and $E_0+\Delta_0$ are correctly given by this model. Also in agreement with the measurements, the outgoing resonance at E_0 is lowered by the interference between the contributions to the deformation potential scattering of the E_0 and $E_0+\Delta_0$ gaps. However, the larger width of the outgoing resonance (see Fig. 2) is not well described by this simple model. It may be due to partial superposition with the ingoing $E_0+\Delta_0$ component.

The model also enables us to check the correct sign of the interference at E_0. It is determined by the relative sign of the matrix elements of the deformation-potential (H_{DP}) and Fröhlich (H_{FI}) electron-phonon interaction. For the 2B terms near E_0 we obtain[10,29]

$$\langle\Gamma_8^v\,|\,H_{DP}\,|\,\Gamma_8^v\rangle\cong d_0\frac{\bar{u}_0}{a_0}>0\ , \tag{5}$$

$$\langle\Gamma_8^v\,|\,H_{FI}\,|\,\Gamma_8^v\rangle\cong -i(\hat{\mathbf{e}}_{LO}\cdot\mathbf{q})(s_e-s_h)_{hh}a_{hh}^2\frac{C_{FI}}{\sqrt{V}}$$
$$-i(\hat{\mathbf{e}}_{LO}\cdot\mathbf{q})(s_e-s_h)_{lh}a_{lh}^2\frac{C_{FI}}{\sqrt{V}}>0\ , \tag{6}$$

where v is the crystal volume, $\bar{u}_0$ the zero-point amplitude of the LO phonon, $\hat{\mathbf{e}}_{LO}$ the polarization vector ($\hat{\mathbf{e}}_{LO}\cdot\mathbf{q}>0$ with our convention for the location of atoms in the primitive cell), and a_{hh} and a_{lh} are the exciton radii of the corresponding light- and heavy-hole states. $s_e-s_h<0$ are effective-mass factors defined in Ref. 9. An estimate for the matrix element in Eq. (5) with respect to that of Eq. (6) yields the ratio 0.30/0.34 in GaP. The relative signs in Eqs. (5) and (6) predict those observed in the interference profiles. We thus expect the dipole-forbidden FI-induced scattering to be as strong in resonance as the DP scattering. We observe, however (Figs. 1 and 4), the DP scattering to be 1 order of magnitude stronger. This must be an artifact of our simplified model.

IV. CONCLUSION

We have shown that interference between the dipole-allowed deformation potential and the dipole-forbidden Fröhlich-intraband Raman scattering by LO phonons occurs near the E_0 and $E_0+\Delta_0$ gaps of GaP. Quantitative interpretation of the data requires a theory which includes electron-hole correlation and exciton-exchange interaction, which is so far lacking. The interference profiles and the corresponding signs of the Raman polarizabilities, however, can be predicted from a simple Lorentzian model based on discrete excitonic transitions.

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