Resonance Raman scattering by optical phonons in GaAs near the E_0 band gap

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We report the resonance of the first-order Raman scattering by longitudinal and transverse optical phonons in GaAs very near to the E_0 band gap at 100 K. The resonance enhancement observed at E_0 for deformation-potential (TO,LO) and Fröhlich-interaction-induced (LO) scattering is about 100 times larger than calculated for uncorrelated electron-hole pairs. The effect is attributed to the Coulomb correlation of discrete and continuum excitons and agrees with Martin's calculation of these effects. The Faust-Henry coefficient is found to be nearly independent of frequency in the region of our measurements ($C=-0.6\pm0.2$).

INTRODUCTION

The investigation of resonance Raman scattering near the lowest direct absorption edge of semiconductors, in particular GaAs, is hampered by the appearance of strong luminescence. Hence most investigations for GaAs have been performed in the neighborhood of the spin-orbit split $E_0+\Delta_0$ direct gap.[1,2] Near this gap, dipole-forbidden scattering by LO phonons, arising from the intraband electron-phonon Fröhlich interaction, has been shown to interfere with dipole-allowed deformation potential and electro-optic scattering in high-purity III-V compounds[1-3] as well as in ternary alloys such as $Ga_{1-x}Al_xAs$.[4] The detailed investigation of the resonance behavior of the interference between allowed and forbidden scattering helps to separate the two contributions to the forbidden Raman scattering by LO phonons.[2-4] The first contribution arises from the **q** dependence of the intraband matrix elements of the Fröhlich interaction, while the second one is of extrinsic origin, probably due to impurity-induced scattering.[2,5-7] Even in high-purity GaAs, it is found that near $E_0+\Delta_0$ only 43% of the forbidden scattering intensity is due to the intrinsic Fröhlich mechanism.[2,4] The theory of resonant Raman scattering (RRS) for uncorrelated electron-hole pairs explains quantitatively the observed resonances and interference effects near $E_0+\Delta_0$.[2,8,9] No need is seen to include the Coulomb correlation of electron-hole pairs[8,9] in the theory of the resonance Raman scattering near $E_0+\Delta_0$. On the other hand, the optical properties are strongly affected by excitonic effects at the fundamental absorption edge E_0 in GaAs and other zinc-blende-type semiconductors.[8,10] Such excitonic effects have already been observed in RRS from GaP, CdS, CuCl, and other bulk materials and multiple quantum wells.[11-14] A number of calculations for allowed and forbidden Raman scattering by optical phonons, including exciton correlations, have already been performed.[8,9] These calculations include the divergences at the bound-exciton energies as poles of Γ functions and require numerical integrations. The most transparent work is probably that of Martin for CdS.[8] Here we will rescale these results in order to apply them to the resonance of GaAs near E_0.

We have investigated experimentally the resonance of deformation-potential scattering by TO and LO phonons very close to the E_0 gap of GaAs as well as that of Fröhlich-interaction-induced forbidden scattering in the spectral range 1.47—1.51 eV, i.e., just below and slightly above the E_0 band gap (1.502 eV). Such resonance Raman data, in a region so close to the E_0 gap of GaAs, have not been available so far.[15] Recently, Beck and Wessel reported on strongly wave-vector-dependent Raman scattering by LO phonons in GaAs near the E_0 gap.[16] Their stimulated Raman gain measurements, performed in the forward-scattering configuration, extend only to excitation energies up to 14 meV below the band gap. These authors conclude that in forward scattering, close to the E_0 resonance, the dipole-allowed scattering by LO phonons is dominant. The extrinsic, impurity-induced contribution to the forbidden scattering is much stronger than the intrinsic **q**-dependent one.

For our measurements we chose high-purity liquid-phase-epitaxy (LPE) GaAs samples ($d\approx50\ \mu$m) similar to those used for the observation of interferences near the $E_0+\Delta_0$ gap.[2,5] Such samples seem to give a minimum contribution from impurity-induced forbidden scattering by LO phonons. For laser energies about 12 meV below the E_0 gap ($\hbar\omega_L\leq1.49$ eV) the absorption coefficient of GaAs is so weak that the Raman signal is not only confined to the epitaxially grown layer but originates also in the substrate. However, the impurity-induced forbidden scattering resonates mainly at outgoing resonances ($\hbar\omega_L=E_0+\hbar\Omega_{LO}$).[2,4] Thus, in the region of investigation ($\hbar\omega_L\simeq E_0$) and under backscattering conditions the impurity-induced scattering should be small.

THEORY

The Raman scattering by TO phonons occurs exclusively through the deformation-potential (DP) electron-phonon interaction.[17] For backscattering at a (110) face the Raman scattering by the LO phonon is not observed. In crossed polarization $x'(y',z')\bar{x}'$ or $x'(z',y')\bar{x}'$ [with $x'=1/\sqrt{2}(1,1,0)$, $y'=1/\sqrt{2}(1,\bar{1},0)$, and $z'=(0,0,1)$] and parallel polarization $x'(y',y')\bar{x}'$ the TO phonon is seen

with the Raman scattering intensity $|a_{\mathrm{TO}}|^2$. The Raman polarizability a_{TO} can be written in terms of contributions of the critical points $E_0-E_0+\Delta_0$ (A_1), $E_1-E_1+\Delta_1$ (A_2), and higher gaps (A_3):[17,18]

$$a_{\mathrm{TO}}=A_1\left\{\frac{2E_0[f(x_0)-f(x_0+\hbar\Omega_{\mathrm{TO}}/E_0)]}{\hbar\Omega_{\mathrm{TO}}}+\frac{4E_0}{\Delta_0}\left[f(x_0)-\left[\frac{E_0}{E_0+\Delta_0}\right]^{3/2}f(x_{0s})\right]\right\}+A_2\left[\frac{1}{1-x_1^2}+\left[\frac{E_1}{E_1+\Delta_1}\right]^2\frac{1}{1-x_{1s}^2}\right]+A_3\ . \quad (1)$$

The function $f(x)$ is defined as

$$f(x)=x^{-2}[2-(1+x)^{1/2}-(1-x)^{1/2}]\ ,$$

where the x variables are "reduced" energies ($x_0=\hbar\omega_L/E_0$, $x_{0s}=\hbar\omega_L/E_0+\Delta_0$, $x_1=\hbar\omega_L/E_1$, $x_{1s}=\hbar\omega_L/E_1+\Delta_1$). A_1 is related to the first-order deformation potential d_0 by[18]

$$A_1=\frac{\sqrt{3}}{128\pi}\frac{a_0^2}{E_0}C_0''\,d_0\ . \quad (2)$$

Here a_0 denotes the lattice constant and C_0'' can be determined from the birefringence induced by a [111] stress.[6,10]

Equations (1) and (2) include in C_0'' a factor of 2, which accounts for light-hole (lh) and heavy-hole (hh) band contributions. Near E_0 the first term of the E_0 contribution in Eq. (1) is enhanced at incoming and outgoing resonance due to the two-band terms of the DP coupling at the E_0 gap.

The dipole-allowed Raman scattering by LO phonons results from the DP-induced electron-phonon interaction and from the electro-optic (EO, interband Fröhlich) coupling of bands via the electric field of the LO phonon.[17] For backscattering at a (001) face, the Raman tensor has the form[2]

$$\vec{\vec{R}}_{\mathrm{LO}}=\begin{pmatrix}0 & a_{\mathrm{LO}} & 0\\ a_{\mathrm{LO}} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}\ . \quad (3)$$

For a_{LO} near E_0 and $E_0+\Delta_0$, an expression similar to Eq. (1) holds with the phonon frequency Ω_{TO} replaced by Ω_{LO}.

The ratio of the dipole-allowed contributions to the Raman scattering by LO phonons due to the DP and EO mechanism is related to the Faust-Henry coefficient C:[17]

$$C=\frac{e_T(\partial\chi/\partial u)}{M^*\Omega_{\mathrm{TO}}^2(\partial\chi/\partial E)}\ . \quad (4)$$

Herein e_T is the transverse dynamical charge, and $M^*=(M_{\mathrm{Ga}}^{-1}+M_{\mathrm{As}}^{-1})^{-1}$ is the reduced mass of the unit cell. $\partial\chi/\partial u$ and $\partial\chi/\partial E$ denote the derivative of the dielectric susceptibility with respect to the relative displacement of the optical phonon and to the electric field, respectively. The Faust-Henry coefficient can be expressed as a function of the Raman polarizabilities for allowed scattering by LO and TO phonons:[17]

$$C=\frac{\Omega_{\mathrm{LO}}^2/\Omega_{\mathrm{TO}}^2-1}{1-a_{\mathrm{LO}}/a_{\mathrm{TO}}}\ . \quad (5)$$

The Fröhlich-interaction-induced (F) intraband Raman scattering by LO phonons yields a diagonal Raman tensor with matrix elements a_F.[2,8,9] The expression for the Raman polarizability a_F near E_0 is similar to the expression obtained near $E_0+\Delta_0$.[2] However, one has to sum up over the contributions from the lh and hh band, the second one being larger than the first. The final expression for a_F then becomes[2]

$$a_F=a_{F,\mathrm{lh}}+a_{F,\mathrm{hh}}$$

with

$$a_{F,j}=\frac{q}{12\pi}\left[\frac{e}{m\hbar}\right]^2\frac{C_F}{\hbar\Omega_{\mathrm{LO}}}\left[\frac{1}{\omega_L}\right]^2\left[\frac{\omega_L}{\omega_S}\right]^{1/2}\times(4V_c\mu_jM^*)^{1/2}\tfrac{2}{3}P^2(s_e-s_h)_jF(\omega_L) \quad (6)$$

and

$$F(\omega)=\left[\left[\frac{\hbar\omega-E_0+i\eta}{\hbar\Omega_{\mathrm{LO}}}\right]^{1/2}-\left[\frac{\hbar\omega-E_0-\hbar\Omega_{\mathrm{LO}}+i\eta}{\hbar\Omega_{\mathrm{LO}}}\right]^{1/2}\right]^3\ . \quad (7)$$

In Eq. (6) $\mathbf{q}$ is the wave vector of the created phonon and, e and m are the free-electron charge and mass, respectively. The reduced mass μ_j is defined as

$$\mu_j^{-1}=m_e^{-1}+m_j^{-1}\ (j=\mathrm{lh},\mathrm{hh})$$

and

$$(s_e-s_h)_j=\frac{m_e-m_j}{m_e+m_j}\ (j=\mathrm{lh},\mathrm{hh})$$

with m_e, m_{lh}, and m_{hh} the effective electron, lh, and hh mass, respectively. V_c is the volume of the primitive cell, and C_F denotes the Fröhlich constant:

$$C_F=\left[2\pi e^2\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right]\hbar\Omega_{\mathrm{LO}}\right]^{1/2}\ , \quad (8)$$

where ϵ_0 and ϵ_∞ are the low (rf)- and high (ir)-frequency dielectric constants. η describes the broadening of the E_0 gap. The Fröhlich-interaction-induced dipole-forbidden scattering resonates strongly near E_0 since it involves only two-band terms [Eq. (6)] and can be considered as a "higher-order" (forbidden) effect.[17]

EXPERIMENTAL PROCEDURE

Both samples studied were n-type undoped epitaxial layers of GaAs grown by liquid-phase epitaxy (LPE). Sample 1 (thickness of the layer $d_1=35$ μm, total thickness of the sample $L_1=360$ μm) was grown on a (001)-oriented substrate of semi-insulating GaAs, whereas sample 2 (thickness of the layer $d_2=59$ μm, thickness of the sample $L_2=620$ μm) was grown on a (110)-oriented sub-

strate. Electrical measurements on sample 1 (same as in Ref. 2) at 77 K yield the carrier concentration $N_D-N_A=n_{77}=10^{13}$ cm^{-3} with the estimated amount of impurities $N_D+N_A=6\times10^{14}$ cm^{-3} ($\rho_{77}=8.7$ Ω cm, $\mu_{77}=100\,000$ cm^2/V s). Sample 2 gave similar values for the resistivity and mobility at 77 K ($\rho=3.5$ Ω cm, $\mu=117\,600$ cm^2/V s). The measurements on sample 1 allowed us to separate the resonance of the dipole-allowed DP scattering and the dipole-forbidden F-induced scattering by LO phonons. On sample 2 the resonance of DP scattering by TO phonons was measured. We used the three different backscattering geometries.

(i) For $z(y,x)\bar{z}$,

$$|a_{\mathrm{LO}}|^2, \quad \text{LO (sample 1)} .$$

(ii) For $z(x,x)\bar{z}$

$$|a_F|^2, \quad \text{LO (sample 1)} . \tag{9}$$

(iii) For $x'(y',z)\bar{x}'$

$$|a_{\mathrm{TO}}|^2, \quad \text{TO (sample 2)} .$$

In these equations x, y, z, x', and y' are parallel to the [100], [010], [001], [110], and [1$\bar{1}$0] directions, respectively.

The Raman measurements were performed with a cw dye laser using Styril 9 (Lambda Physik, Göttigen) pumped with all lines of an argon-ion laser (≃6.0 W). It lased in the range of 1.45–1.55 eV. The power of the incident laser beam was typically between 40 and 60 mW. The power density on the sample was kept below 10 W/cm^2 using a slit focus on the sample. The samples were mounted on a cooled finger of a liquid-nitrogen cryostat. The temperature was determined to be (100±5) K.

In order to display our results in absolute values of the Raman scattering intensity $|\hat{e}_S\cdot\vec{\vec{R}}\cdot\hat{e}_L|^2$ we used the sample substitution method.[17] We chose high-purity silicon as a reference [$|a|=27$ Å^2 at 1.5 eV (Ref. 19)]. The experimental scattering rates outside the crystal relative to silicon $R'_{\mathrm{GaAs}}/R'_{\mathrm{Si}}$ were corrected for absorption, refractive index, and reflectivity according to the expression[2,7]

$$R'=\left[\frac{T_S T_L}{n_S n_L}\frac{\omega_S^3}{M^*\Omega_{\mathrm{ph}}V_c}[n(\Omega_{\mathrm{ph}})+1]\frac{1-e^{-(\alpha_L+\alpha_S)L}}{(\alpha_L+\alpha_S)}\right]\times P'_L\frac{\Delta\Omega'}{2c^4}|\hat{e}_S\cdot\vec{\vec{R}}\cdot\hat{e}_L|^2 . \tag{10}$$

Here R' is the scattering rate, $\Delta\Omega'$ the solid angle for collection outside the crystal, and P'_L the power flux of the incident laser light. $T_L(T_S)$, $n_L(n_S)$, and $\alpha_L(\alpha_S)$ denote the transmission coefficient, refractive index, and absorption coefficient at the frequency of the laser (scattered) light $\omega_L(\omega_S)$, respectively. Ω_{ph} is the frequency of the optical phonon TO or LO and $n(\Omega_{\mathrm{ph}})$ the phonon occupation number. The absorption coefficients for Si were taken from Ref. 20. For the absorption correction of GaAs we shifted the results of Sturge[21] measured at 90 K by 3.5 meV towards lower energies to account for the temperature difference of 10 K. The total thickness of the thinnest sample was 360 μm. Thus the exponential function in Eq. (10) must only be applied for GaAs on the low-energy side of the resonance ($\hbar\omega_L\leqq1.478$ eV). For $\hbar\omega_L\geqq1.49$ eV ($\alpha\approx300$ cm^{-1}) the *outgoing* signal is essentially confined to the epitaxial layer. The total error resulting from these corrections is estimated to be about 50%, mainly due to the uncertainty of the Raman polarizability of Si and of the absorption coefficient of GaAs near the band edge.

RESULTS AND DISCUSSION

Figure 1 shows the resonance in the three different backscattering configurations [Eq. (9)]. Measurements above E_0 ($\hbar\omega_L\geqq1.505$ eV) are prevented by strong luminescence. The dotted curves depict the result of calculations for DP + EO and F-induced scattering by LO phonons [Eqs. (1) and (6)] in absolute units. The dashed and solid curves will be discussed later. The parameters of these calculations, listed in Table I, are chosen the same as obtained from the interference at $E_0+\Delta_0$.[2,4] For the DP (TO) and DP + EO (LO) scattering the observed resonance is similar. It increases by a factor of 250 as one approaches the E_0 gap and then decreases. The forbidden F-induced scattering resonates stronger (increase of a factor of 1500) and decreases also above the gap. Interference effects of the type observed for $E_0+\Delta_0$ are rather weak at E_0 and will not be discussed here. Over the whole resonance we determine the ratio of dipole-allowed contributions to LO- and TO-phonon scattering to be nearly constant ($|a_{\mathrm{LO}}/a_{\mathrm{TO}}|^2=1.6\pm0.2$). With Eq. (5) we obtain the Faust-Henry coefficient $C=-0.6\pm0.2$. It is in good agreement with the value −0.57 measured at 1.0 eV,[27] and with a calculation by Bell (−0.77).[28] At 1.47 eV the Raman polarizability a_{TO} of the TO phonon

TABLE I. Parameters for the calculation of DP- and F-induced Raman scattering by LO phonons according to Eqs. (1) and (6).

$E_0=1.502$ eV	[a]
$E_0+\Delta_0=1.842$ eV	[b]
$\eta(E_0)=2.0$ meV	
$\eta(E_0+\Delta_0)=3.5$ meV	[b]
$E_1=3.028$ eV	[c]
$E_1+\Delta_1=3.246$ eV	[c]
$\hbar\Omega_{\mathrm{LO}}=36.3$ meV	[d]
$\hbar\Omega_{\mathrm{TO}}=33.7$ meV	[d]
$m_e=0.067\ m$	[e]
$m_{so}=0.16\ m$	[e]
$m_{\mathrm{lh}}=0.082\ m$	[e]
$m_{\mathrm{hh}}=0.47\ m$	[e]
$P^2/m=12.9$ eV	[f]
$C_F=2.14\times10^{-5}$ eV cm$^{1/2}$	[g]
$\epsilon_0=13.1$	[h]
$\epsilon_\infty=11.1$	[i]
$A_1=8$	[b]
$A_2=26$	[b]
$A_3=-3$	[b]

[a] $E_0+\Delta_0-0.34$ eV.
[b] Reference 4.
[c] Reference 22.
[d] Reference 23.
[e] Reference 24.
[f] $P=\hbar(2\pi/a_0)$.
[g] From Eq. (8).
[h] Reference 25.
[i] Reference 26.

(away from the strong resonance) amounts to 93 Å^2, as compared with previously reported values of 63 ± 10 Å^2 at 1 eV (Ref. 29) and 50 Å^2 at 1.2 eV (Ref. 30).

The comparison of the dotted curves, calculated without electron-hole correlations, with the experimental data gives clear evidence that the resonance enhancement near E_0 is much stronger than predicted by this theory. Below 1.47 eV, however, this theory is known to represent well the experiments.[18] Between 1.47 and 1.502 eV the enhancement of the experimental data with respect to this theory amounts to a factor of 125 for DP + EO scattering and to a factor of 106 in the case of F-induced scattering. The enhancement factor must be interpreted as related to e-h Coulomb interaction. The enhancement near E_0 due to Coulomb-correlated e-h pairs with respect to uncorrelated e-h pairs can be estimated, within the effective-mass exciton (Wannier) model, with the help of Ref. 8. We will try to rescale the data of Martin (Figs. 2 and 3 of Ref. 8) calculated for DP- and F-induced scattering in CdS to account for excitonic effects in GaAs, since the excitonic properties are different in CdS and GaAs (see Table II). Since the $1s$-exciton binding energy in GaAs is small [$E_{1s}=4.2$ meV (Ref. 31)], the main contribution to RRS is expected from exciton effects in the interband continuum. On this continuum the imaginary part ϵ_i of the dielectric function near E_0 has a step given by (in atomic units $e=\hbar=m=1$)[35]

$$\epsilon_i(E_0)=\frac{2\pi}{E_0}\mathcal{F}(2\mu^*)^{3/2}\,|E_{1s}|^{1/2}\,, \tag{11}$$

where E_0 is the energy of the direct gap, E_{1s} the $1s$-exciton binding energy, and $\mathcal{F}$ the oscillator strength:[35]

$$\mathcal{F}=\frac{P^2}{E_0}=\frac{1}{E_0}\left[\frac{2\pi}{a_0}\right]^2. \tag{12}$$

By taking the values of Table II, the exciton enhancement of the absorption is about 0.254 times lower for GaAs than for CdS. This prefactor should enter as a square into the Raman intensity. The enhancement for the Raman polarizability of DP scattering in CdS can be read from Fig. 2 of Ref. 8. At 12 meV ($0.4E_{1s}$ of CdS) below E_0 we get a factor of 16 for the ratio of the total Raman polarizability (discrete and continuum exciton contribution) with respect to that of uncorrelated e-h pairs. This value yields a total enhancement of the Raman scattering *intensity* for DP (+ EO) scattering by LO phonons in GaAs of $(16\times0.254)^2\simeq16$. Experimentally we obtain a factor of 14 at $\hbar\omega_L=1.49$ eV (12 meV below the E_0 gap). The exciton enhancement of F-induced scattering can be deduced from Fig. 3 of Ref. 8. Comparing the total contribution and that of uncorrelated pairs 12 meV below the E_0 gap one reads a factor of 32.5 for CdS which is rescaled to $(32.5\times0.254)\simeq8$ for the Raman polarizability of GaAs. This gives an enhancement factor of 64 for the Raman intensity which compares well with our observed factor of 42 (cf. Fig. 1). This good agreement, while possibly partly fortuitous, shows that the order of magnitude of the scattering efficiency can be predicted by application of Martin's theory including e-h Coulomb correlation near a three-dimensional critical point. Recently, the observation of strongly wave-vector-dependent resonant Raman scattering by LO phonons in GaAs near the E_0 band gap was reported.[16] The authors applied Martin's theory for intrinsic bulk DP- and q-dependent F-induced Raman scattering for correlated electron-hole pairs (Fig. 2 of Ref. 16). We tried to compare their calculations for DP- and F-induced backscattering with our experimental data in Fig. 2. We scaled their curves, given in arbitrary units, to the observed scattering intensities at 1.472 eV. The agreement between the calculations and the experimental points (triangles and solid curve in Fig. 2) is good for the forbidden scattering up to 1.49 eV. At 12 meV below the E_0 gap ($\hbar\omega_L=1.49$ eV), the observed dipole-forbidden

TABLE II. Comparison of exciton parameters of CdS and GaAs used to rescale Martin's calculations of cross sections.

	CdS	GaAs
E_{1s}	30 meV[a]	4.2 meV[d]
μ^*	0.16 m[a]	0.058 m[e]
E_0	2.57 eV[b]	1.50 eV
a_0	5.82 Å[c]	5.65 Å[f]

[a]Reference 8.
[b]Reference 32.
[c]Reference 33.
[d]Reference 31.
[e]Reference 24.
[f]Reference 34.

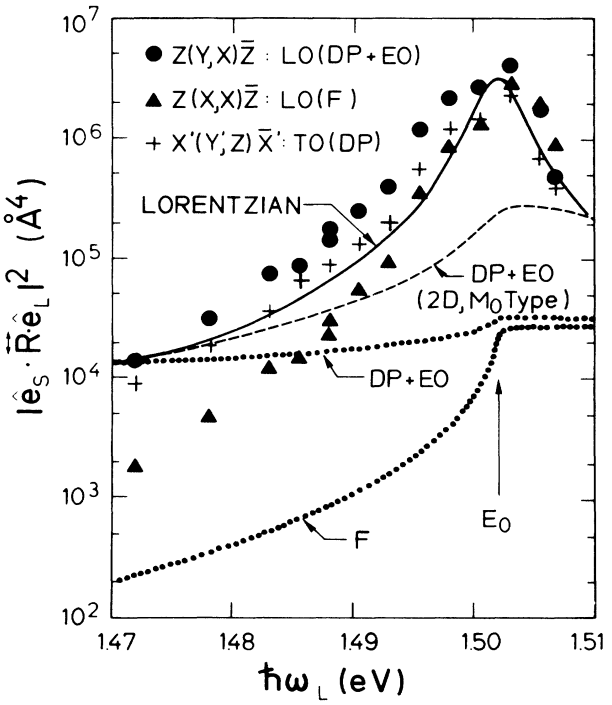

FIG. 1. Resonance curves for the dipole-allowed (DP, DP + EO) scattering by TO and LO phonons and for the dipole-forbidden scattering (F) by LO phonons near the E_0 gap. The dotted curves are calculated from theory assuming uncorrelated electron-hole pairs. The dashed curve is calculated assuming that E_0 corresponds to a two-dimensional critical point [Eq. (13)]. The solid curve is a Lorentzian function for the Raman intensity [Eq. (14)].

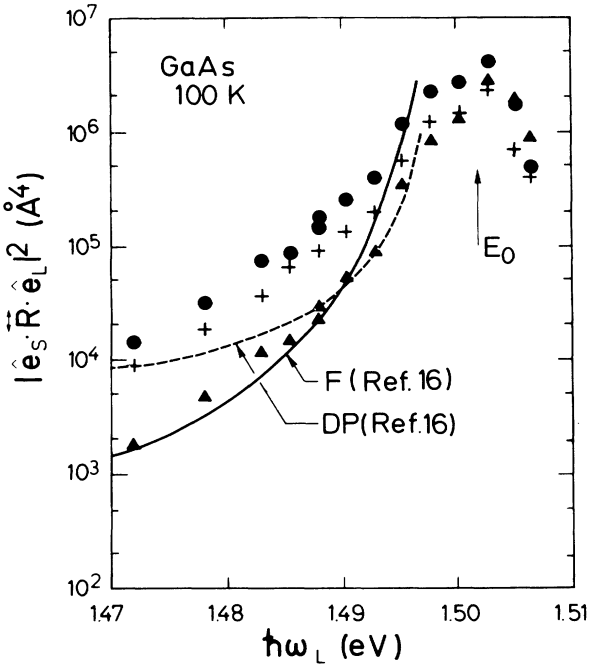

FIG. 2. Comparison of our experimental data with calculated curves published by Beck and Wessel (Ref. 16) based on Martin's theory, incorporating Coulomb-correlated pairs.

scattering is about one-fifth of the dipole-allowed one, in agreement with Ref. 15. As one approaches E_0, the calculated F scattering becomes even stronger than the DP scattering. The theory, however, predicts too strong an increase for F-induced scattering near E_0, a fact which may be attributed to exciton lifetime broadening and, possibly, to polariton effects.[9] The allowed scattering resonates more strongly than the calculations of Ref. 16 even below 1.49 eV. Our scaling arguments, however, gave in this region reasonable agreement with experiment. Since no details of the calculation were given in Ref. 16, we cannot comment any further on the reasons for this apparent discrepancy.

There is yet another simple way to simulate the effect of the exciton continuum and the higher discrete states on the RRS at the E_0 gap. Guided by the fact that the excitons change the density of electronic transitions near the E_0 band gap from $E^{1/2}$-type to a step function, E_0 can be regarded as a two-dimensional critical point (M_0 type), and the calculations of Raman intensity can be performed, in a heuristic way, with the uncorrelated e-h pairs as intermediate states:[10,17,35]

$$|\hat{e}_S \cdot \vec{R} \cdot \hat{e}_L|^2 \propto \left| \ln \left[\frac{\hbar\omega_L - E_0 + i\eta}{\hbar\omega_L - E_0 - \hbar\Omega_{LO} + i\eta} \right] \right|^2 . \quad (13)$$

The dashed curve in Fig. 1 shows the result of a calculation, in arbitrary units, with Eq. (13) using the parameters of Table I and fitted to the experiment at 1.472 eV. The agreement between the experimental data and the calculated curve is definitely better than the (DP + EO)-based dotted curve found with E_0 as a three-dimensional critical point. The discrepancy between the data and the dashed curve can perhaps be attributed to the contribution of the $n=1$ discrete exciton to the resonance enhancement. To estimate this contribution, it is reasonable to take a Lorentzian function for the Raman intensity:

$$|\hat{e}_s \cdot \vec{R} \cdot \hat{e}_L|^2 \propto \frac{1}{(\hbar\omega_L - E_0)^2 + \eta^2} . \quad (14)$$

The solid line in Fig. 1 shows the intensity evaluated with Eq. (14) (in arbitrary units) using the values of E_0 and η given in Table I (also fitted at 1.472 eV). The agreement between the calculated curve and the data is remarkable. We realize, however, that the effects of the discrete and continuum excitons cannot be rigorously represented this way. Accurate calculations of the scattering cross section for the band parameters of GaAs, including exciton interaction, are thus needed.

We should point out that the corresponding resonance enhancements are considerably larger in the II-VI compounds[13] than in GaAs, a fact which can be attributed to the stronger intensity of the edge excitons in those materials.

To summarize, we have measured the resonance enhancement of the Raman intensities of the optic phonons very close to the fundamental absorption gap E_0 of GaAs at low temperatures. The comparison of the data with theory, incorporating uncorrelated electron-hole pairs as intermediate states, clearly demonstrates the dominant contributions of excitonic effects. An estimate of the order of magnitude of these effects made from Martin's results[8] agrees with our observations. However, a detailed comparison of the experiments with the calculated curves by Beck and Wessel, based on Martin's theory (Fig. 2) reveals some discrepancies. It would be worthwhile to restudy the theory of RRS with polaritons as intermediate states[36] and make a quantitative comparison with the experimental data. Also, a detailed theory of impurity-induced scattering by excitons via Fröhlich interaction is needed.

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