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Doubly and triply resonant Raman scattering by LO phonons in GaAs/AlAs superlattices

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We report measurements on a GaAs/AlAs superlattice with a splitting between the $n=1$ heavy- and light-hole bands nearly equal to the energy of two LO phonons. This condition produces triply resonant Raman scattering (three real intermediate states). The combinations of phonons and the polarization of this resonance can be explained by the dispersion of the phonons of B_2 symmetry and the mixing between the hole bands. In one-phonon scattering we attribute a shift in the resonance between the two polarization configurations to doubly resonating impurity-induced Fröhlich scattering.

For GaAs/AlAs superlattices the optical-phonon branches of the two constituents do not overlap. Hence, "confined" optical modes result. Different experiments have confirmed this[1-3] and have shown that the optical modes with **k** vector along the growth direction of the superlattice (z) fit well into the dispersion relation of the bulk crystal for wave vectors $m\pi/(n+1)a$, where m is an integer and the layer consists of n monolayers of thickness a.[3,4] In the D_{2d} point group of the superlattice these modes belong either to the A_1 (m even) or to the B_2 (m odd) representations. The A_1 phonons couple with the electron system via Fröhlich interaction and the B_2 phonons via the deformation potential.[3] Therefore the B_2 phonons should appear in the $z(x,y)\bar{z}$ configuration and the A_1 phonons in the $z(x,x)\bar{z}$ configuration. This is the case far from resonances with electronic transitions, but near resonance the A_1 modes dominate, even for $z(x,y)\bar{z}$.[3,5] Impurity-induced Fröhlich-interaction scattering[6] was proposed to explain this behavior.[7]

The superlattice periodicity leads to the lifting of the heavy- and light-hole band degeneracy which is obtained for $k=0$ in the bulk crystal. The splitting between these minibands can be tuned to be equal to the energy of one LO phonon by choosing the appropriate well thickness. Thus the conditions for doubly resonant Raman scattering, where both intermediate states are real, are fulfilled.[8,9] The same can be achieved in bulk GaAs under uniaxial stress.[10] If the induced splitting is equal to the energy of two LO phonons, triply resonant second-order scattering, where all three intermediate states are real, becomes possible.[11]

In this paper we present measurements on a GaAs/AlAs superlattice with the splitting between the $n=1$ heavy- and light-hole bands equal to the energy of two LO phonons (triple-resonance condition). We observe combinations of A_1 phonons in both configurations [$z(+,+)\bar{z}$ and $z(+,-)\bar{z}$], the intensity being strongest in the $z(+,-)\bar{z}$ configuration. This remarkable and unexpected effect can be traced back to the dispersion of the B_2 phonons and to mixing between the two hole bands for directions perpendicular to z. We have also measured resonance profiles for first-order scattering. They peak at different positions for the two scattering configurations. We attribute this to doubly resonating impurity-induced Fröhlich interaction. It has been known but not understood that only A_1 phonons are observed near resonance for both polarization configurations (B_2 phonons appear off resonance in the depolarized case).[3] Our work offers a natural explanation in terms of impurity- and Fröhlich-interaction-induced double resonance.

The sample used for our measurements was a GaAs/AlAs superlattice grown by molecular-beam epitaxy on a (001)-oriented semi-insulating GaAs substrate with 100 periods of 28-Å-thick GaAs and 28.6-Å AlAs (as determined by x-ray diffraction). This sample was chosen among others because the splitting between the $n=1$ heavy- and light-hole bands was 67 meV, close to the energy of two LO phonons (72 meV). That splitting was determined by photoluminescence excitation: $E_{1h}=1.873$ eV and $E_{1l}=1.940$ eV, where E_{1h} (E_{1l}) is the transition energy from the $n=1$ heavy- (light-) hole band to the $n=1$ conduction band. Photoluminescence and Raman spectra were excited with a cw DCM (4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran) dye laser and recorded with a Spex spectrometer using photon counting. We used a line focus and circularly polarized light in the backscattering configuration along z. The sample temperature was $\cong 100$ K. We took the areas under the peaks as a measure of the scattering intensity.

In the resonance Raman spectra we observe a number of peaks, LO$_m$, due to confined LO phonons, a broad structure due to AlAs-like interface modes,[12] overtones of confined LO phonons, and a combination of the AlAs-like interface modes with LO phonons, all superimposed on the luminescence due to the E_{1h} transition. For a laser energy far from resonance [Fig. 1(a)] we see the odd LO$_m$ modes for $z(y,x)\bar{z}$ and the even LO$_m$ modes for $z(x,x)\bar{z}$. [LO$_1$ at 295.5 ± 0.5 cm^{-1}, LO$_2$ at 292 ± 1 cm^{-1}, LO$_3$ at 289.5 ± 0.5 cm^{-1}, LO$_4$ at 286 ± 1 cm^{-1}, LO$_5$ at 281.5 ± 1 cm^{-1}, LO$_6$ at 276.5 ± 1.5 cm^{-1}, in agreement with the phonon dispersion of GaAs.[13]] The peak at 268.5 ± 2 cm^{-1} for $z(x,x)\bar{z}$ is assigned to the symmetry-forbidden TO phonon.[4,14] Under outgoing resonance with the E_{1h} transition for the LO$_2$ phonon [Fig. 1(b)] we see

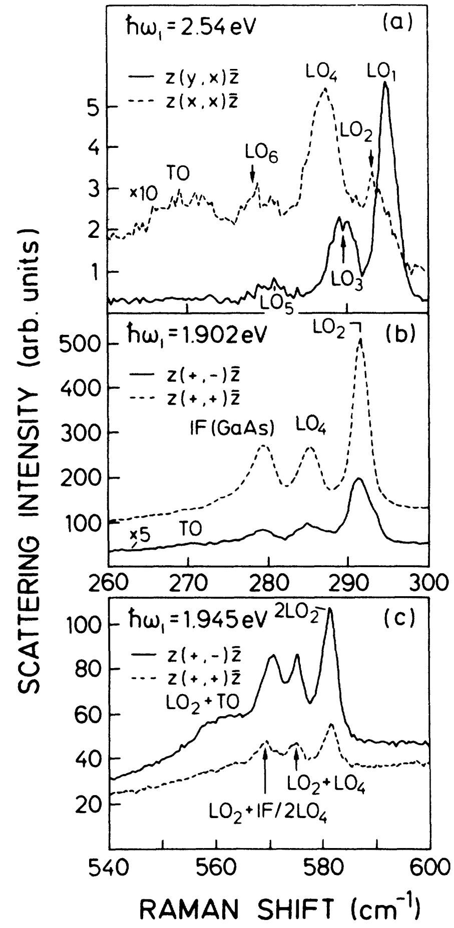

FIG. 1. 28-Å GaAs/28.6-Å AlAs superlattice. (a) and (b) First-order scattering. (a) Off-resonance Raman spectra for $z(y,x)\bar{z}$ and $z(x,x)\bar{z}$. (b) Raman spectra for $z(+,-)\bar{z}$ and $z(+,+)\bar{z}$ in outgoing resonance with the E_{1h} transition. (c) Second-order scattering. Raman spectra for $z(+,-)\bar{z}$ and $z(+,+)\bar{z}$. Triple-resonance conditions. "+" and "−" are with respect to fixed axes and not related to the direction of propagation.

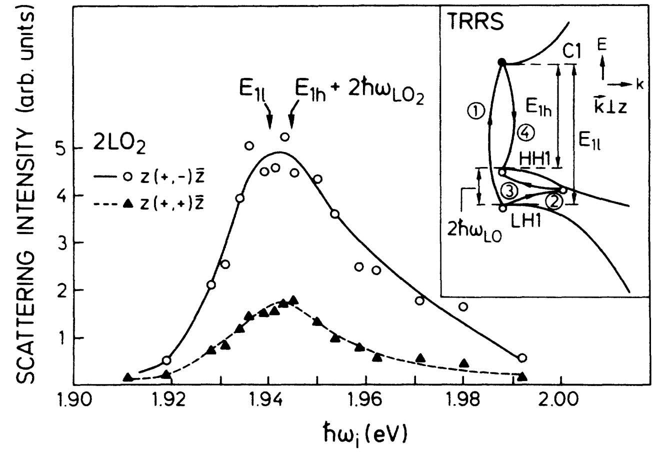

FIG. 2. Resonance profiles of the two-LO_2-phonon line for $z(+,-)\bar{z}$ and $z(+,+)\bar{z}$. The lines are drawn as a guide to the eye. The inset shows the scattering diagram for triply resonant Raman scattering (TRRS). The four steps indicated correspond to the four matrix elements in Eq. (1).

only even modes for both $z(+,-)\bar{z}$ and $z(+,+)\bar{z}$.[3,5] The LO_2 (LO_4) peak appears at 291 (285) cm^{-1}. Thus there are indications of a 1-cm^{-1} downshift, as observed in Ref. 5. There is a third peak at 278.5 ± 0.5 cm^{-1}, which lies between the values of the LO_5 and LO_6 phonons as determined far from resonance. If we assign this peak to the LO_6 mode, we do not obtain good agreement with the GaAs dispersion: The energy difference between this and the LO_4 peak is smaller than that between LO_4 and LO_2, while the dispersion in bulk GaAs increases for increasing wave vector near the center of the Brillouin zone. Hence we assign it to GaAs-like interface (IF) modes.[12] In Fig. 1(c) we show the two-LO-phonon region for triple-resonance conditions. In both configurations we observe three peaks at 582, 576, and 569 cm^{-1} which can be assigned to two-LO_2-phonon, LO_2+LO_4-phonon, and LO_2+IF-phonon or two-LO_4-phonon combinations, respectively. For $z(+,-)\bar{z}$ the peak at 560 ± 1 cm^{-1} corresponds to the LO_2+TO-phonon combination.

The only possible process leading to stress-induced triply resonant second-order scattering is shown in the inset of Fig. 2:[11] (1) An electron is excited from the first light-hole band into the first conduction band. (2) A phonon with wave vector **q** is created and interband scattering of the hole into the first heavy-hole band takes place via deformation-potential interaction. (3) Then a second phonon with wave vector −**q** is created and the hole is scattered via intraband Fröhlich interaction. (4) Finally, the electron-hole pair recombines. For appropriate **q**'s all three intermediate states are real.

For these processes we would expect to see combinations of one B_2 and one A_1 phonon under conditions of triple resonance. However, we only observe combinations of A_1 phonons. In second-order scattering all wave vectors of one of the phonons are allowed. Furthermore, recent calculations show that there is a large dispersion in the

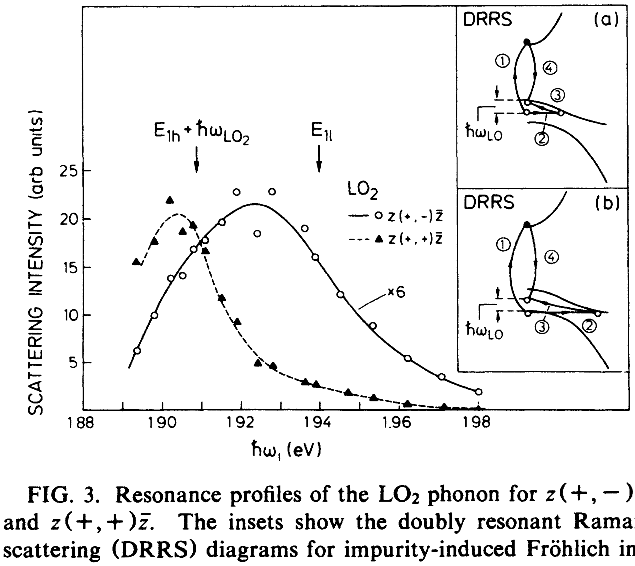

FIG. 3. Resonance profiles of the LO_2 phonon for $z(+,-)\bar{z}$ and $z(+,+)\bar{z}$. The insets show the doubly resonant Raman scattering (DRRS) diagrams for impurity-induced Fröhlich interaction scattering (a) in outgoing resonance with the E_{1h} transition and (b) in incoming resonance with the E_{1l} transition.

frequency of B_2 modes for small wave vectors with directions between parallel and perpendicular to z (see Fig. 1 of Ref. 15) due to the different macroscopic fields associated with these (interfacelike) modes, while the A_1 modes are practically dispersionless.[15] Therefore, since all directions of the one-phonon wave vector are allowed, the B_2 modes smear out. This is probably the reason why only A_1 phonons were seen by Sood, Menéndez, Cardona and Ploog[16] even off resonance.

Scattering by two even phonons is possible via two Fröhlich-induced interactions, and therefore normally appears for $z(+,+)\bar{z}$.[16] But as can be seen in Fig. 2, the scattering intensity is stronger for $z(+,-)\bar{z}$. The same unexpected behavior is seen for all phonon combinations. This effect can be traced back to the mixing between heavy- and light-hole bands for $\mathbf{k}\neq 0$ and perpendicular to z.[17] Perturbation theory yields for the amplitude of the iterated electron–one-phonon Fröhlich scattering the following expression:[18]

$$\frac{\langle g|H_{E\text{-}R}|0\rangle_{h\,h}\langle 0|H_F|k\rangle_{h\,h}\langle k|H_F|0\rangle_{l\,l}\langle 0|H_{E\text{-}R}|g\rangle}{(\hbar\omega_i-E_{1l})[\hbar\omega_i-\hbar\omega_{\mathrm{ph}}-E_{1h}-\Delta E_{1h}(k)](\hbar\omega_s-E_{1h})} \tag{1}$$

where $\omega_{i(s)}$ are the frequencies of the incident (scattered) light, $\Delta E_{1h}(k)$ the dispersion of the heavy-hole band, $H_{E\text{-}R}$ the electron-radiation Hamiltonian, H_F the Fröhlich Hamiltonian, and $|g\rangle$, $|0\rangle_l$, $|k\rangle_h$, and $|0\rangle_h$ are the wave functions of the ground state, an excited state with a hole in the light-hole band at $\mathbf{k}=\mathbf{0}$, same with the hole in the heavy-hole band at $\mathbf{k}=\mathbf{q}$, or in the heavy-hole band at $\mathbf{k}=\mathbf{0}$, respectively. If we assume that the incident "+" circularly polarized light couples with the $x+iy$ part of the $|0\rangle_l$ wave function, then

$$_h\langle k|H_F|0\rangle_l=\left\langle a\left[\frac{1}{\sqrt{2}}(x-iy)\downarrow\right]+b\left[\sqrt{2/3}z\uparrow-\frac{1}{\sqrt{6}}(x+iy)\downarrow\right]\middle|H_F\middle|\sqrt{2/3}z\uparrow-\frac{1}{\sqrt{6}}(x+iy)\downarrow\right\rangle=b\langle x|H_F|x\rangle\neq 0 \tag{2}$$

and

$$_h\langle 0|H_F|k\rangle_h=\left\langle\frac{1}{\sqrt{2}}(x-iy)\downarrow\middle|H_F\middle|a\left[\frac{1}{\sqrt{2}}(x-iy)\downarrow\right]+b\left[\sqrt{2/3}z\uparrow-\frac{1}{\sqrt{6}}(x+iy)\downarrow\right]\right\rangle=a\langle x|H_F|x\rangle\neq 0\,, \tag{3}$$

since the Fröhlich interaction can only couple nonorthogonal functions and spin must be conserved. (a and b depend on the degree of mixing between the light- and heavy-hole bands: $a^2+b^2=1$.) Thus, the scattered light has circular polarization opposite to that of the incident one. Furthermore, coupling between the light- and heavy-hole bands becomes possible also via Fröhlich interaction [only for $z(+,-)\bar{z}$] and triple resonance obtains. For $z(+,+)\bar{z}$, coupling between the light- and heavy-hole bands is not possible via Fröhlich interaction. Therefore, the triple-resonance conditions are not fulfilled and we observe a weaker double resonance.[19]

The valence bands in the inset of Fig. 2 represent semiquantitatively typical cases as shown in Ref. 20. The band anticrossing, at which the mixing should be $a=b\approx 0.7$, occurs close to the intermediate state for the triple resonance. Hence the mixing seems sufficient to explain qualitatively the results reported here.

We have also measured resonance profiles for first-order scattering. The results for the LO_2 phonon are shown in Fig. 3. For $z(+,+)\bar{z}$ there is a peak at the outgoing resonance with the E_{1h} transition. For $z(+,-)\bar{z}$ there is a broader peak between the outgoing resonance with E_{1h} and the incoming one with E_{1l}. (We observe the same for the LO_4 phonon and also for the GaAs- and AlAs-like interface phonons.) Gant *et al.*[5] also reported differences in peak positions for the two configurations but did not explain them. Here we attribute this effect to impurity-induced Fröhlich interaction:[6] The hole is scattered twice, once elastically due to the hole impurity and once due to the hole-phonon interaction. Hence we have a fourth-order process with three intermediate states, with all phonon wave vectors allowed. For outgoing resonance with E_{1h} [inset (a) of Fig. 3] two intermediate states are real, thus we have a double resonance.[19] For incoming resonance with E_{1l} [inset (b)] we also have double resonance with two real intermediate states because the mixing between the two hole bands for $\mathbf{k}\neq 0$ renders the impurity-induced coupling between them possible (as in the two-phonon case). We propose that these two resonances are not resolved, thus leading to one peak at an intermediate position. This assumption is supported by the fact that the resonance profile for $z(+,-)\bar{z}$ is much broader than for $z(+,+)\bar{z}$. This intermediate resonance is not possible for $z(+,+)\bar{z}$ even if impurity-induced Fröhlich interaction is the scattering mechanism (as in the case of interface phonons), because it is not possible to have the first intermediate state belonging to the light-hole band and the last one to the heavy-hole band for this configuration [see Eqs. (2) and (3)].

In summary, we have observed triply resonant second-order Raman scattering by A_1 phonons via iterated electron–one-phonon Fröhlich interaction. It becomes possible because of the mixing between heavy- and light-hole bands. We have also observed unresolved incoming and outgoing resonances with the E_{1l} and E_{1h} transitions, respectively, due to doubly resonating impurity-induced Fröhlich scattering. This mechanism also explains why only A_1 phonons are seen at resonance for any polarizations.[3]

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