Optical Vibrational Modes and Electron-Phonon Interaction in GaAs Quantum Wells

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We have discovered phonons active in resonant Raman scattering from GaAs quantum-well heterostructures that are actually the optical vibrations of a thin ionic slab. These modes are revealed by selection rules for the polarizations of incident and scattered light that are different from those of bulk GaAs. Analysis of the Raman tensor indicates new deformation-potential electron-phonon scattering processes which are a direct consequence of the reduced symmetry of the layered system.

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The electromagnetic boundary conditions which apply at semiconductor surfaces are the source of many interesting physical effects, such as surface[1] and guided wave[2] phonon polaritons. In these phenomena the normal modes of bulk excitations are significantly altered by the presence of a dielectric interface. GaAs-AlGaAs multilayer heterostructures present an excellent system in which to study such effects because of the high quality of the interfaces. In Raman scattering from GaAs-AlAs superlattices the observed frequencies of optical phonons were interpreted in terms of the anisotropic dielectric constant of a layered continuum.[3] Similar experiments on GaAs-AlAs superlattices showed a zone folding of acoustic phonons which was accounted for in the elastic continuum limit.[4,5]

In this paper we present Raman measurements on GaAs-AlGaAs quantum-well heterostructures which cannot be accounted for within a continuum model. In these experiments light is resonant with quasi-two-dimensional exciton states confined to the GaAs quantum wells. Thus the vibrational properties of *individual* ~100-Å-thick layers are probed. In contrast to all previous Raman studies, which were done in backscattering from the layers, we report right-angle scattering from heterostructures. For the first time Raman scattered light propagating in the layer plane and polarized along the superlattice axis has been observed. We find optical phonons which are distinct from those predicted by continuum theories of layered media. Although these vibrations occur at bulk frequencies, the selection rules for the polarizations of incident and scattered light are completely contrary to those of an infinite crystal. In fact these selection rules are characteristic of the normal modes of a thin ionic crystal slab. The slab modes bear the surprising property that a transverse vibration occurs at the bulk longitudinal optic (LO) frequency, while the longitudinal mode occurs at the bulk transverse optic (TO) frequency.[6] Vibrations with this behavior were detected in the infrared absorption of thin (4000 Å) alkali-halide films.[7] The present study represents the first identification of light scattering by such vibrational modes in a semiconductor superlattice.

In addition to the unique vibrational properties, our experiments show direct evidence of modifications in the electron-phonon interaction by the reduction in crystal symmetry. We show that the observed polarization selection rules for scattering at the transverse optic frequency can only be accounted for by admitting new deformation-potential matrix elements which are not present in bulk GaAs.

Our right-angle scattering geometry (shown in the inset to Fig. 1) is made possible by enclosing the multilayer heterostructure in AlGaAs cladding layers ~1 μm thick. The cladding forms a waveguide[8] for the scattered light. In these experiments the incident light ($\hbar\omega_i \sim 1.55$ eV) is in resonance with the $n=1$ heavy-hole exciton, a state

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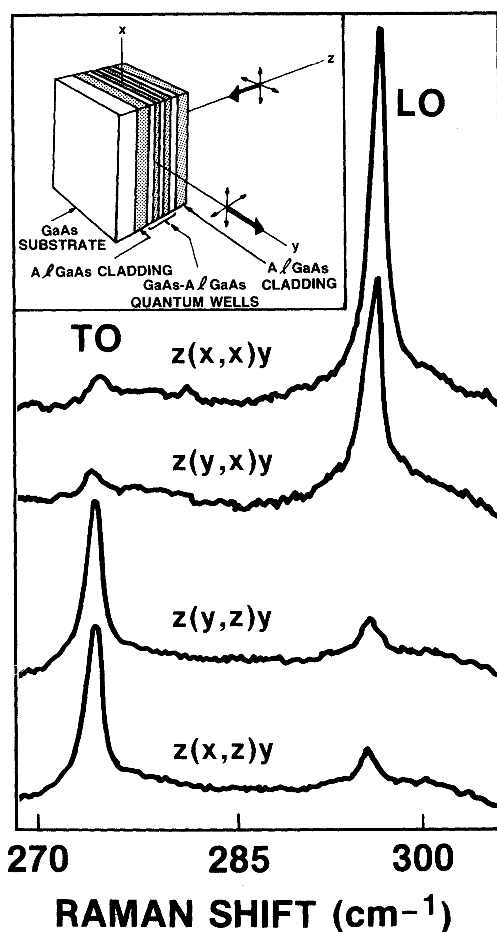

FIG. 1. Right-angle Raman spectra. Incident photon energy is 1.55 eV. Propagation directions for incident and scattered light are labeled by first and last letters, with the respective polarizations in parentheses. Inset shows the geometry for right-angle scattering. (001) is along z.

formed from the lowest subbands of the quantum well.[9] Since the scattered frequency ω_S is Raman downshifted from the exciton energy, negligible absorption occurs in the waveguide. We present data for a sample in which 65 periods of 96-Å-GaAs–98-Å-$(Al_{0.28}Ga_{0.72})As$ are enclosed by two 1.45-μm $(Al_{0.28}Ga_{0.72})As$ cladding layers. All measurements were made with the sample immersed in liquid helium at $T\sim 2$ K. The sample was oriented with the x and y axes along the cleavage directions (110) and $(1\bar{1}0)$. Right-angle scattering in other crystal orientations was done on several samples. However, it was found that the spectra are the same for x and y along *any* two mutually perpendicular axes in the plane of the layers. Thus we find that the Raman tensor which relates the polarizations of incident and scattered light is invariant under rotations about the superlattice axis.

Figure 1 shows the right-angle Raman spectra. The scattering occurs at the TO and LO frequencies of bulk GaAs. Contrary to what might be expected on the basis of an anisotropic dielectric continuum model,[3,10] there is no evidence of structure at any intermediate frequencies, nor at any frequencies related to the AlGaAs phonons. The striking feature of the data is the clear polarization selection rule. When both incident and scattered polarizations are in the plane of the layers, the dominant scattering is at the LO frequency. However, scattering at the TO frequency dominates the spectra in which the scattered light is polarized along the superlattice axis.

As is well known from standard lattice dynamics, the splitting between TO and LO frequencies in a polar crystal is caused by the presence of the long-range Coulomb interaction. While vibrations at the TO frequency reflect only short-range forces, those at the LO frequency are also accompanied by a macroscopic electric field. Polarization selection rules for TO scattering by the *short-range* forces are determined by the transformation properties of the zone-center phonons and of the electronic states under operations of the crystal point group. For the D_{2d} symmetry of the GaAs quantum well, the nonzero components of the Raman tensor for a phonon displacement u_P relating scattering $(\hat{\epsilon}_S)$ to incident $(\hat{\epsilon}_L)$ polarizations correspond to $|e_{PLS}|$, the Levi-Civita symbol expressed along the cubic axes.[11] Thus there is a unique correspondence between the polarizations observed in TO scattering and the direction of ionic displacement responsible for the scattering: $(y,z)\leftrightarrow u_x$; $(x,z)\leftrightarrow u_y$. We now consider these ionic vibrations u_x,u_y in the context of the quantum-well geometry. These modes, which occur exactly at the frequency of the bulk GaAs phonon, cannot propagate in the direction normal to the layers because of the alternation of materials in the heterostructure. Thus the phonon propagation vector $\vec{q}$ lies entirely along y, and one would expect vibrations $u_y \parallel \vec{q}$ to occur at the longitudinal frequency and $u_x \parallel \vec{q}$ at the transverse frequency. However, as shown above u_x and u_y *both* occur at the transverse frequency. This indicates that although the optical vibrations of the GaAs quantum well occur at the same frequencies as in the bulk material, the structure of the modes is fundamentally different.

The modification of the bulk modes which occurs in the 100-Å-thick GaAs quantum well may be interpreted in terms of the electromagnetic boundary conditions at the AlGaAs-GaAs interface. When the crystal film thickness L is such that $qL \ll \pi$,

as is the case in these experiments where $q \sim 3 \times 10^5$ cm^{-1}, the polarization associated with phonon displacements is slowly varying in the x-y plane. Then the continuity conditions on the normal component of $\vec{D}$ and the tangential component of $\vec{E}$ force those vibrations which are parallel to the layers to produce no electric field, and those vibrations along the normal to produce no electric displacement. Thus in-plane ionic vibrations occur at the transverse frequency, and vibrations normal to the layer at the longitudinal frequency.[6,7] Departure from these bulk optical frequencies is expected only when the thickness of the film becomes comparable to the wavelength of the vibration. In the present experiments, the condition $q \gg \omega_{TO}/c$ is also satisfied, so that the effects of retardation, i.e., polariton modes, need not be taken into account.[12]

Raman scattering at the TO frequency reflects only the short-range deformation-potential electron-phonon interaction. However, the macroscopic electric field associated with vibrations at the LO frequency leads to an additional scattering mechanism via the Fröhlich interaction. In the present work we fix our attention on the scattering at the TO frequency and consider the effects of reduced dimensionality on deformation-potential matrix elements.

The cross section for Raman scattering resonant with exciton state $|1\rangle$ is proportional to

$$|\hat{\epsilon}_S \cdot \vec{R} \cdot \hat{\epsilon}_L|^2 \sim \left| \sum_n \frac{\langle 0|\vec{p}\cdot\hat{\epsilon}_S|n\rangle\langle n|H_{dp}|1\rangle\langle 1|\vec{p}\cdot\hat{\epsilon}_L|0\rangle}{(\omega_L-\omega_1)(\omega_S-\omega_n)} \right|^2,$$

where $\langle p\rangle$ are dipole matrix elements for exciton absorption and emission and $\langle H_{dp}\rangle$ is the deformation-potential matrix element. We need only consider matrix elements of H_{dp} among the conduction and uppermost valence bands. Since the conduction-band edge in GaAs is s-like ($|jm_j\rangle = |\frac{1}{2} \pm \frac{1}{2}\rangle$), it is not affected by the deformation-potential interaction. The valence bands transform like a $j=\frac{3}{2}$ quadruplet. In bulk GaAs the fourfold degeneracy is spin-orbit split at $k \neq 0$ into light ($|\frac{3}{2} \pm \frac{1}{2}\rangle$) and heavy ($|\frac{3}{2} \pm \frac{3}{2}\rangle$) holes. The deformation potential produces no coupling between these valence states.[13–15] In quantum wells the superlattice axis lifts the valence-band degeneracy at $k=0$ and quantizes the angular momenta of the bands along (001).[16] Therefore for the hole states in quantum wells, polarization $\hat{\epsilon}_S \parallel z$ ($\Delta m_j = 0$) corresponds to optical transitions of light-hole excitons while $\hat{\epsilon}_L \parallel x$ or y ($\Delta m_j = 1$) corresponds to heavy-hole excitons. Thus the fact that the heavy-hole-exciton resonance is accompanied by scattered light polarized along z implies a deformation-potential coupling between light and heavy holes.

We now examine how a deformation-potential coupling between light and heavy holes which does not exist in bulk GaAs might arise in quantum wells. The phonon normal coordinates for ionic displacements u_x, u_y, u_z transform in the same way under the symmetry operations of the crystal point group as the off-diagonal components of a traceless symmetric second-rank tensor. Thus from the theory of invariants[14] we can write the Hamiltonian as

$$H_{dp} \sim u_x\{J_y,J_z\} + u_y\{J_x,J_z\} + u_z\{J_x,J_y\},$$

where the brackets denote anticommutators of the components of total angular momentum. In the layered quantum-well structure, the reduced symmetry forces the quantization of the angular momenta along the (001) superlattice axis. This particular basis leads to the matrix elements

$$H_{dp}(u_x) \sim \begin{pmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{pmatrix}, \quad H_{dp}(u_y) \sim \begin{pmatrix} -\sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix},$$

$$H_{dp}(u_z) \sim \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix},$$

where the σ_i are the Pauli matrices. Rows and columns correspond to $m_j = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ of the fourfold degenerate valence band. The nonvanishing components of the Raman tensors are found by combining these matrix elements with the selection rules for absorption and emission of light. For vibrations along z, they are identical for the light- and heavy-hole excitons: $[(R_h(u_z)]_{xy} = [R_h(u_z)]_{yx} = [R_l(u_z)]_{xy} = [R_l(u_z)]_{yx} \sim \frac{1}{2}$. However, for vibrations along x and y the nonzero tensor components differ: $[R_h(u_x)]_{zy} = [R_h(u_y)]_{zx} \sim 1$ for the heavy-hole resonance, but $[R_l(u_x)]_{yz} = [R_l(u_y)]_{xz} \sim 1$ for the light-hole resonance.

These Raman tensors are in agreement with the $z(x,z)y$ and $z(y,z)y$ spectra for incident light resonant with the heavy-hole exciton. The coupling of light and heavy holes by the deformation potential successfully accounts for the observed polarization selection rules for scattering at the TO frequency. In addition, this coupling predicts that TO scattering of incident light resonant with the light-hole exciton should not be observed in the present experimental geometry, where incident light propagates along z. In fact our experiments support this prediction. If any such scattering exists, it is present at a level less than 15% of that at the

heavy-hole-exciton resonance. This marked asymmetry which occurs between the light- and heavy-hole-exciton resonances is an effect which has been widely predicted[11,17] but never before observed in semiconductors.

In conclusion, we have discovered phonons active in Raman scattering from GaAs-AlGaAs heterostructures which are actually the optical vibrations of a thin ionic slab. In our experiments light scattering is resonant with a spatially confined, rather than an extended, electronic excitation. Thus our spectra are most sensitive to vibrational modes that are localized within the GaAs layer. Polarization properties of the scattering reveal an interband matrix element for the quantum-well deformation-potential electron-phonon interaction which does not exist in bulk GaAs. We show how this interband process arises as a result of the reduced symmetry of the heterostructure, and that it is described by an asymmetric Raman tensor.

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