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Second-order Raman scattering by confined optical phonons and interface vibrational modes in GaAs-AlAs superlattices

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The second-order Raman spectrum of the confined GaAs-like optical phonons in a GaAs-AlAs superlattice is reported. For laser energies in resonance with the first exciton in the GaAs quantum wells, the experiments show a series of sharp peaks that can be attributed to combinations of confined phonons of A_1 symmetry. An additional broader peak corresponds to the combination of the GaAs-like and AlAs-like interface vibrational modes previously reported in the first-order spectra. The resonance profile of the overtones and combinations of confined phonons is also presented.

Under resonant conditions, Raman scattering by longitudinal optical (LO) phonons in polar semiconductors can be observed in scattering configurations which are forbidden according to the dipole selection rules.[1] This phenomenon is due to the **q**-dependent (**q** is the phonon wave vector) contribution of the Fröhlich electron-phonon interaction to the Raman efficiency. While the phonon wave vector is small in first-order scattering[2] due to conservation of crystal momentum, the pairs of phonons which participate in the corresponding second-order process are only subject to the restriction that the *sum* of their wave vectors must be nearly zero. Thus, phonons with arbitrary wave vectors can participate in second-order Raman scattering. This additional degree of freedom allows for double resonances, which dramatically enhance the Raman efficiency; theory[3] predicts the Fröhlich-interaction-induced scattering by two LO phonons to be stronger than its first-order counterpart. This has actually been observed in GaP,[4] CdTe,[5] and GaAs.[6] Only for the case of impurity-induced intraband Fröhlich Raman scattering by LO phonons[2] (a process which is formally similar to Raman scattering by two LO phonons[5]) first- and second-order intensities become of comparable magnitude.

The results obtained for bulk materials suggest that Raman scattering by two LO phonons is an excellent candidate for the study of second-order Raman scattering in semiconductor superlattices. This paper reports for the first time such measurements for a GaAs-AlAs superlattice.

Raman experiments in the backscattering configuration were performed for (001)-oriented GaAs-AlAs superlattices grown by molecular-beam epitaxy. We present here results for one sample with $d_1 = 20$ Å and $d_2 = 60$ Å (d_1 and d_2 are the thicknesses of the GaAs and AlAs slabs, respectively). The period $d = d_1 + d_2$ was repeated 400 times. The results for other samples with different d_1 and d_2 are qualitatively similar to the ones given here. The temperature of the sample during the measurements was ~ 10 K. The spectra were excited with a DCM dye laser (supplied by Lamda Physik, Göttingen, FRG) pumped with a cw Ar^+ laser. The scattered light was analyzed with a Jarrell Ash double monochromator and detected by photon counting.

Figure 1 shows the first-order Raman spectrum in the region corresponding to the optical phonons of GaAs. The peaks labeled LO_m correspond to the confined (sometimes improperly called "folded") optical phonons.[7,8] These are modes localized in the GaAs slabs, equivalent to those vibrations in the bulk material whose wave vector is given by $q = m\pi/d_1$. In the D_{2d} point group of the superlattice, the odd values of m correspond to phonons belonging to the B_2 representation, while the even values denote A_1-type phonons. The peak IF_1 has been attributed to an interface mode.[9] In contrast with the confined phonons, which are localized in either slab, the interface vibrations imply some polarization in both materials. A second interface mode, which we call IF_2, can be seen with a Raman shift corresponding to the optical phonon frequencies in AlAs. This peak resonates strongly with the excitons localized in the GaAs slabs,[9] thus demonstrating the interface character of the vibration.

The A_1 modes dominate the spectra taken with the laser light in resonance with the first electron–heavy-hole exciton in the GaAs quantum wells (solid line in Fig. 1). The B_2 modes can only be seen far from resonance and in a scatter-

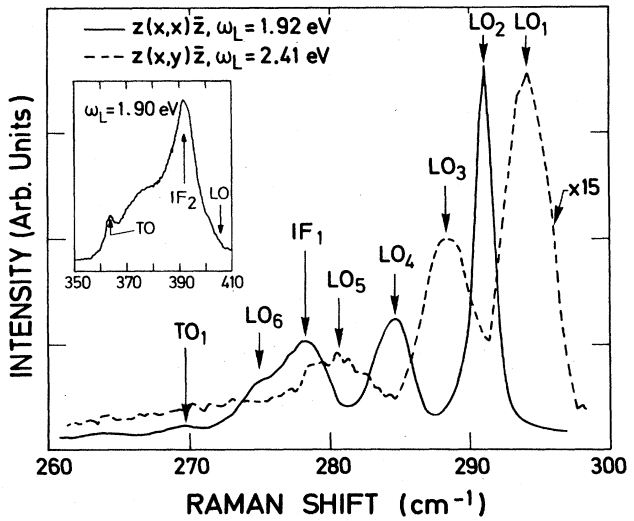

FIG. 1. First-order Raman spectrum of the confined LO phonons in a GaAs-AlAs superlattice with $d_1 = 20$ Å, $d_2 = 60$ Å. The different peak widths are due to the different spectrometer resolutions in the resonant case (solid line) and the off-resonance case (dashed line). The inset shows the Raman spectrum in the region of the AlAs-like optical phonons (Refs. 8 and 9).

ing configuration which is allowed for Raman scattering induced by the deformation-potential-type electron-phonon interaction.[1] This alternation of the modes is due to their different types of coupling with the electronic system. The most strongly resonant contribution to the Raman efficiency is given by the intraband matrix elements of the Fröhlich electron-phonon interaction.[1,8] These matrix elements are of the form

$$\int_{-d_1/2}^{d_1/2} dz \cos^2\beta z \times \begin{cases} \sin(m\pi z/d_1) & (m=1,3,5,\ldots) \\ \cos(m\pi z/d_1) & (m=2,4,6,\ldots) \end{cases} \quad (1)$$

since the electronic wave functions are of the form $\psi \propto \cos(\beta z)$, where $\beta^2 = 2mE/\hbar^2$, E being the electron-level energy. The Fröhlich potential V_F can be deduced by noting that the relative atomic displacements, given by[10]

$$u_{\rm rel} \propto \cos(m\pi z/d_1) \quad (B_2 \text{ modes, } m \text{ odd}) \ ,$$
$$u_{\rm rel} \propto \sin(m\pi z/d_1) \quad (A_1 \text{ modes, } m \text{ even}) \ , \quad (2)$$

are proportional to the gradient of V_F. Equation (1) means that the matrix element cancels for B_2 modes, thus explaining why only A_1 modes are seen in resonance.

Figure 2 shows Raman spectra in the region corresponding to the second-order spectrum of the GaAs optical branches. The spectrum in the lower part of the figure was taken near resonance. The Raman structure rides on a photoluminescence background. The most interesting feature (also shown in the triangular inset) is the set of sharp peaks which we attribute to combinations of the peaks seen in Fig. 1. However, as can be observed by comparing the measured frequencies for the first- and second-order spectra, the combinations LO_1+LO_1 and LO_1+LO_2 are missing. In fact, all the second-order peaks can be explained as combinations of A_1 modes (m even). The absence of B_2 modes in the resonance spectrum is due to the same matrix-element cancellation discussed for the first-order spectra. The theoretical expression for the second-order Raman efficiency[3] has an additional intraband matrix element of the Fröhlich interaction, i.e., it is of fourth order in perturbation theory,[3] because *two* phonons must be created. Thus, the only nonvanishing contributions are those in which neither of the two Fröhlich matrix elements involve B_2 phonons. Figure 3 shows the resonance behavior of the A_1-phonon combinations. It displays the typical characteristics of the double-resonance effects:[3,5,11] a dominant outgoing resonance and an asymmetric general shape, with stronger scattering efficiencies to higher energies. This is due to the fact that double resonances are only possible when the laser frequency is in the continuum ($\omega_L > \omega_1 + 2\Omega_{\rm LO}$, where ω_L is the laser frequency, ω_1 the exciton energy, and $\Omega_{\rm LO}$ the LO-phonon frequency). All these aspects of the Raman scattering by two confined phonons closely resemble what occurs in bulk material. However, as found in the first-order spectra,[8] the peaks in resonance are seen for all scattering configurations.

An additional interesting feature in the second-order spectra is the broad peak labeled IF_1+IF_2. This peak exactly corresponds to the sum of the interface modes IF_1 and IF_2 of Fig. 1.

In the off-resonance spectra (upper part of Fig. 2) we expect to see all possible combinations of confined phonons because now the contribution of the deformation-potential interaction cannot be neglected. However, the combinations LO_1+LO_1 and LO_2+LO_2 also seem to be missing in the off-resonance case. We believe that this is an apparent effect due to the shift of the second-order Raman peak as a function of the laser energy. This phenomenon has also

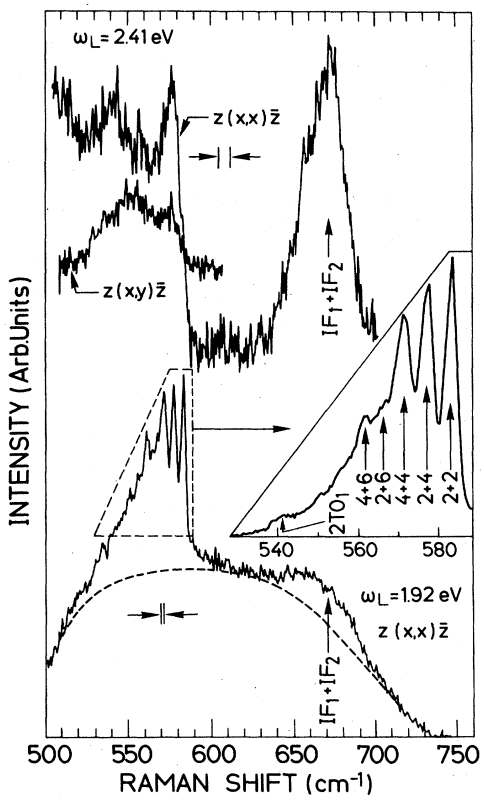

FIG. 2. Second-order Raman spectrum of the same superlattice as in Fig. 1. The numbers assigned to the peaks in the inset correspond to the subindexes in Fig. 1.

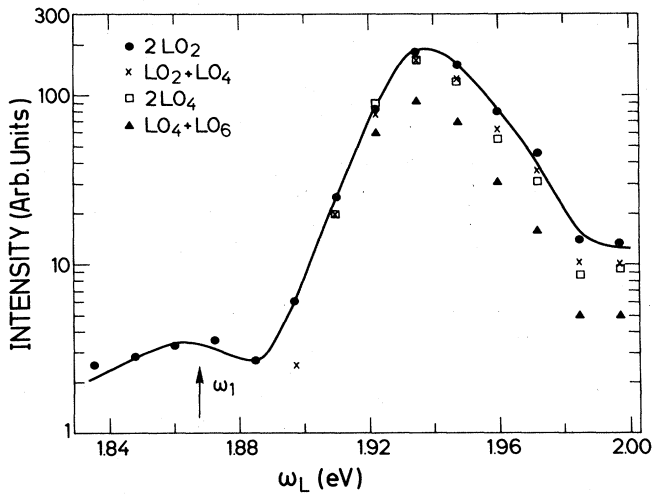

FIG. 3. Resonance of the Raman efficiency for some of the phonon combinations shown in Fig. 2. No absorption correction has been applied.

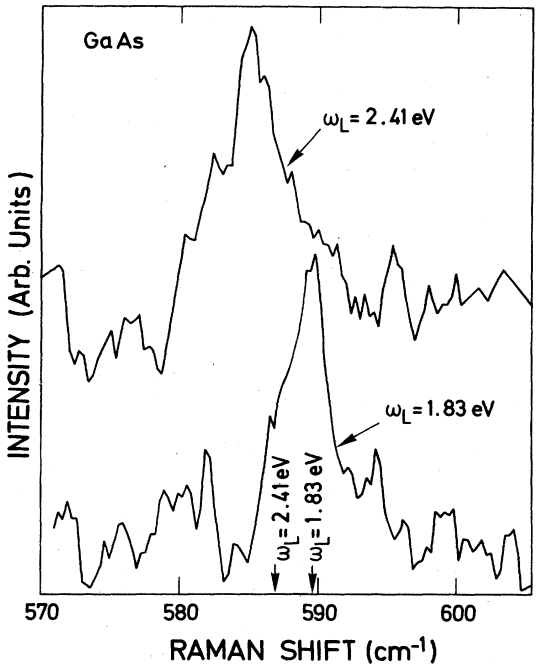

FIG. 4. Two-LO-phonon Raman spectrum of bulk GaAs (temperature ~ 10 K) for two different laser energies. The arrows denote the calculated peak positions.

been observed in bulk GaAs.[11] In Fig. 4 we show two-LO-phonon spectra of bulk GaAs for laser energies close and far above the $E_0+\Delta_0$ gap (~ 1.85 eV). Although the peaks are very weak compared with those of the superlattices, a relative shift of ~ 5 cm^{-1} is apparent. The arrows show theoretical predictions using Zeyher's theory,[3] assuming that the dominant contribution arises from the $E_0+\Delta_0$ gap and taking $M_{LO}=530$ as the "effective" LO-phonon mass.[11,12] The reason for the decrease of the peak energy is that the double-resonance process, which dominates the Raman efficiency, implies a real transition between two electronic states with emission of a phonon. Because the electronic bands display a parabolic dispersion, when the laser energy increases larger phonon wave vectors are needed to keep the electronic transition real. These larger phonon wave vectors correspond to lower phonon frequencies, as can be seen in the phonon dispersion curves for the LO branch.[12] Hence we believe that all phonon combinations are present in the second-order spectrum out of resonance but shifted with respect to the values calculated from Fig. 1. They cannot be clearly resolved due to the larger slit width used to detect this weak spectrum. The off-resonance spectrum in the $z(x,x)\bar{z}$ configuration is also similar to the Γ_1 component of the second-order spectrum of bulk GaAs,[13] thus suggesting that the second-order electron-phonon Hamiltonian (deformation potential) also plays an important role.

In summary, we have reported the most prominent features of the second-order Raman spectrum of GaAs-AlAs superlattices, which in resonance are determined by the Fröhlich electron-phonon interaction. Second-order Raman structure induced by the deformation potential interaction is also seen out of resonance. This opens up the interesting possibility of studying the effect of zone folding (in particular, the folding of the acoustic branches) on the two-phonon density of states.

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[1]M. Cardona, in *Light Scattering in Solids II,* edited by M. Cardona and G. Güntherodt, Topics in Applied Physics, Vol. 50 (Springer, Berlin, 1982), p. 19, and references therein.

[2]Except in impurity-induced Raman scattering. See A. A. Gogolin and E. I. Rashba, Solid State Commun. **19**, 1177 (1976).

[3]R. Zeyher, Phys. Rev. B **9**, 4439 (1974).

[4]B. A. Weinstein and M. Cardona, Phys. Rev. B **8**, 2795 (1973).

[5]J. Menéndez, M. Cardona, and L. K. Vodopyanov, Phys. Rev. B **31**, 3705 (1985).

[6]W. Kauschke and M. Cardona (unpublished).

[7]B. Jusserand, D. Paquet, and A. Regreny, Phys. Rev. B **30**, 6245 (1984); C. Colvard, T. A. Grant, M. V. Klein, R. Merlin, R. Fischer, H. Morkoc, and A. C. Gossard, *ibid.* **31**, 2080 (1985).

[8]A. K. Sood, J. Menéndez, M. Cardona, and K. Ploog, Phys. Rev. Lett. **54**, 2111 (1985).

[9]A. K. Sood, J. Menéndez, M. Cardona, and K. Ploog, Phys. Rev. Lett. **54**, 2115 (1985).

[10]G. Kanellis, J. F. Morhange, and M. Balkanski, Phys. Rev. B **28**, 3406 (1983). This result, obtained from a microscopic lattice-dynamics approach, implies a vanishing of the phonon displacements at the interface, and differs from the macroscopic electrostatic model of R. Fuchs and K. L. Kliewer, Phys. Rev. **140**, A2076 (1965). A discussion of this problem is given in Ref. 8.

[11]D. Olego and M. Cardona, Solid State Commun. **39**, 1071 (1981).

[12]G. Dolling and J. L. T. Waugh, in *Lattice Dynamics,* edited by R. F. Wallis (Pergamon, London, 1965), p. 19.

[13]R. Trommer and M. Cardona, Phys. Rev. B **17**, 1865 (1978).