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Light scattering determination of band offsets in GaAs-$Al_xGa_{1-x}As$ quantum wells

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The conduction-band offset in GaAs-$Al_xGa_{1-x}As$ quantum wells is determined with a new light scattering method. A value of $\Delta E_c/\Delta E_g = Q_e = 0.69$ is found for $x \simeq 0.06$. The conduction-band discontinuity ΔE_c is obtained from *electronic* light scattering in a photoexcited sample. The total gap discontinuity ΔE_g is deduced from resonance Raman scattering by $Al_xGa_{1-x}As$ phonons in the same sample. The light scattering method is unique because ΔE_c can be determined regardless of the valence-band structure or exciton binding energies. It also allows a direct measurement of ΔE_g, so that an exact knowledge of the alloy composition in $Al_xGa_{1-x}As$ is no longer needed.

The determination of band offsets in semiconductor heterojunctions is of great current interest.[1] The most thoroughly studied system in the last years has been the GaAs-$Al_xGa_{1-x}As$ heterojunction. The pioneering optical absorption studies of Dingle, Gossard, and Wiegman[2] were interpreted in terms of a conduction-band discontinuity $\Delta E_c = 0.85\Delta E_g$, where ΔE_g is the energy gap difference between $Al_xGa_{1-x}As$ and GaAs. However, later work by Miller and co-workers[3,4] in parabolic and square quantum wells indicates a conduction-band offset of $Q_e = \Delta E_c/\Delta E_g = 0.6$. This more symmetric distribution of the discontinuities between the conduction and valence bands has been confirmed by a number of electrical[5-11] and optical[12-14] experiments. A closer analysis of the available optical data, however, indicates that within the overall convergence to $Q_e \sim 0.6$, a considerable broad range of values $0.5 \lesssim Q_e \lesssim 0.65$ has to be used in order to fit all the published data.[15] This is related to the experimental uncertainties in ΔE_c and ΔE_g. The discontinuity ΔE_c is obtained from a fit of the optical transition energies. This is a difficult procedure which requires a knowledge of exciton binding energies and a calculation of the sublevel structure in the conduction and valence bands. The uncertainties in ΔE_g arise from the estimate of the Al concentration x and from the interpolation formulas used to evaluate the $Al_xGa_{1-x}As$ energy gap.

In this Rapid Communication, we report a new experimental approach to the band-offset problem which eliminates the main sources of error discussed above. We use inelastic light scattering by photoexcited electrons in GaAs quantum wells to determine the intersubband transition energies in the conduction band.[16] From this experiment we obtain an accurate value of ΔE_c. Unlike the methods based on exciton spectroscopy, the light scattering determination of ΔE_c does not require a calculation of the complicated[17] valence-band structure or an estimate of exciton binding energies. The experimental uncertainties associated with the determination of ΔE_g are also completely bypassed by deducing this value from the position of the first delocalized exciton.[18] This exciton, formed by levels just above the barriers, leads to sharp resonances in the Raman scattering by phonons confined in the barrier material.[18]

We investigated samples designed to have wide GaAs quantum wells and barriers with low aluminum concentration. This choice was made in order to keep the thickness uncertainty below 1%, while the lowest energy levels remain sensitive to the Q_e value. On the other hand, the effective-mass theories (including nonparabolicity effects[19]) and the square-well aproximation are expected to be more accurate for samples with low x and relatively wide wells.

We present data for sample A, which has ten periods of alternating GaAs layers (thickness $d_1 = 334 \pm 3$ Å) and $Al_xGa_{1-x}As$ layers (thickness $d_2 = 459 \pm 3$ Å). The Al concentration is expected to be $x \sim 0.06$. The thicknesses were determined from transmission electron microscopy (TEM) measurements.

The sample was placed in a He cryostat and kept in contact with flowing He gas ($T \sim 8$ K). A dye laser operated with DCM was used simultaneously to photoexcite electrons and as a light scattering probe. The beam was focused onto the sample by means of a spherical high-quality lens. Typical power densities were in the range of 2×10^3 W/cm^2. Stokes–anti-Stokes ratios suggest electron temperatures of the order of 30 K. The phonon Raman experiment was carried out with an LD-700 dye laser.

Figure 1 shows light scattering spectra for sample A. The laser energy is near the $E_0 + \Delta_0$ gap of GaAs, for which the intensity of electronic light scattering is expected to show resonant enhancements.[20,21] The peaks are assigned to different intersubband transitions between the first four levels in the conduction band of the GaAs quantum wells. These levels are indicated by subindices 0,1,2,3. The assignment is confirmed by the resonant behavior observed in the three spectra shown in Fig. 1. As expected,[20,21] the transitions involving higher levels resonate for higher laser energies.

The presence of an electron-hole plasma can affect the intersubband transition energies in two different ways: by modifying the square-well potential if the electron and hole charge densities do not cancel out, and by the macroscopic electric fields set up by charge-density fluctuations.[20,21] The latter appear for the polarized configuration (parallel incident and scattered light polarizations) and can be avoided by taking the spectra—as in Fig. 1—in the depolarized configuration (perpendicular incident and scattered polarizations) which corresponds to spin-density fluctuations of single-particle character.[20,21] The cancellation of the total charge density can be demonstrated by the independence of the depolarized spectra upon laser power density.[22] This situation is different from that in modulation-doped samples, where charge separation occurs and the bare quantum-well potential is deeply modified.[21] Our results also suggest that many-body effects on the transition energies, which should

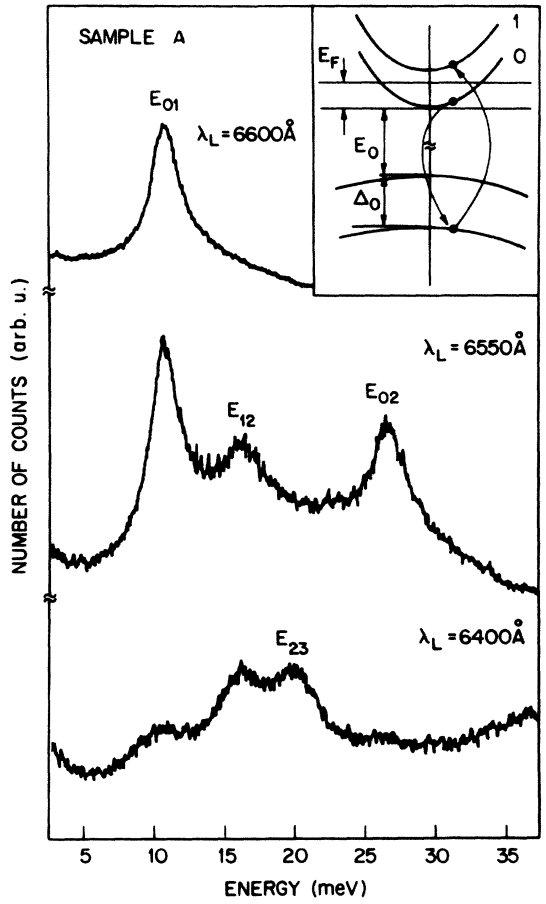

FIG. 1. Depolarized light scattering spectra (Stokes shift) for three different laser wavelengths. The inset shows schematically the two-step microscopic process responsible for the light scattering.

be a function of the electron density,[23] are negligible in our samples.

The experimental transition energies are summarized in Table I. The absolute conduction-band discontinuity can be deduced from a calculation of the energy-level structure in the conduction band. Because of the high experimental accuracy, it is important to take band nonparabolicity into account. To that extent we use the effective-mass equations of Pötz, Porod, and Ferry,[15] which include the split-off band and remote band effects. These equations lead to energy-dependent masses and boundary conditions, but can be easily solved by looking for self-consistency between the input parameters and those which result from the calculated eigenvalues. We take the necessary band-structure data from Ref. 19. To fit the intersubband transitions we consider ΔE_c as adjustable parameter and also vary d_1 within the uncertainty limits of the TEM measurement. The best fit is obtained for $\Delta E_c = 55.9$ meV and $d_1 = 335.1$ Å.

The calculated transition energies shown in Table I agree with the measured values within experimental error.[24] It should be emphasized at this point that the equations in Ref. 15, which we have used in our calculations, include the effect of the p-antibonding conduction band as a perturbation. It has been shown by Rössler[19] that in bulk GaAs this approach is correct for energies below 50 meV from the conduction-band minimum. This is just the energy of the highest confined level in our samples. For higher levels, the coupling to the p-antibonding conduction band has to be treated exactly. This consideration might be relevant for experiments in thinner wells.[14] The difference between calculated and measured intersubband transitions is displayed in Fig. 2 for different choices of ΔE_c.

Having established the value of ΔE_c, we can calculate Q_e from a determination of the total gap discontinuity ΔE_g. We use resonance phonon Raman scattering at delocalized excitons[18] to measure ΔE_g. While the excitons localized in the GaAs quantum wells only produce resonances in Raman scattering by phonons confined in the same wells,[25] the delocalized excitons lead to sharp resonances in the Raman scattering by phonons in the barrier material as well.[18]

Figure 3 shows the resonance behavior of the LO_1 phonon of $Al_xGa_{1-x}As$ in sample A as a function of laser ener-

TABLE I. Experimental and theoretical intersubband transitions in the conduction band of sample A. All values are in meV.

	E_{01}	E_{12}	E_{23}	E_{02}
Expt.	10.42 ±0.2	16.03 ±0.3	19.92 ±0.3	26.59 ±0.2
Theory[a]	10.29	16.25	19.89	26.55

[a]For $\Delta E_c = 55.9$ meV and $d_1 = 335.1$ Å.

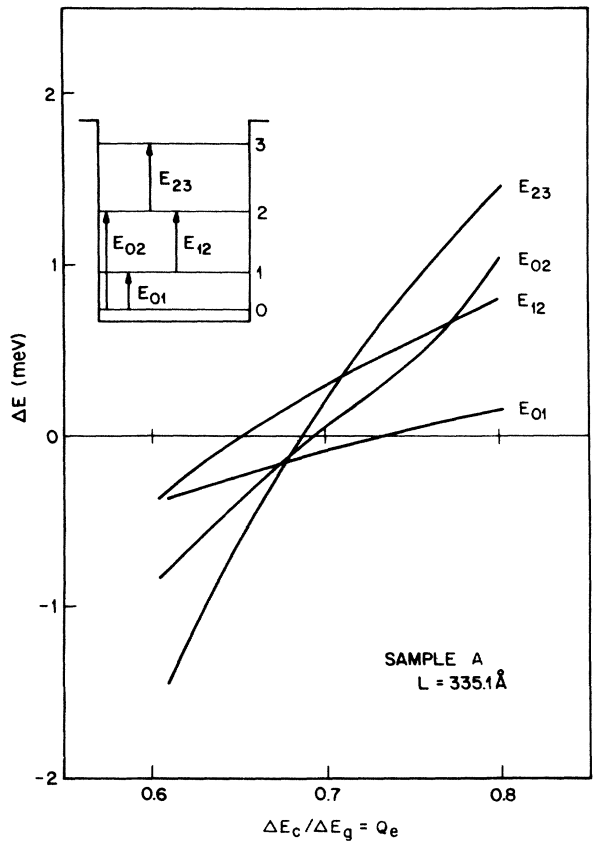

FIG. 2. Deviation between theoretical and experimental values of the intersubband transition energies as a function of ΔE_c. The values of ΔE_c are given in terms of $Q_e = \Delta E_c/\Delta E_g$, taking $\Delta E_g = 81$ meV (see text). The inset shows a schematic representation of the investigated transitions.

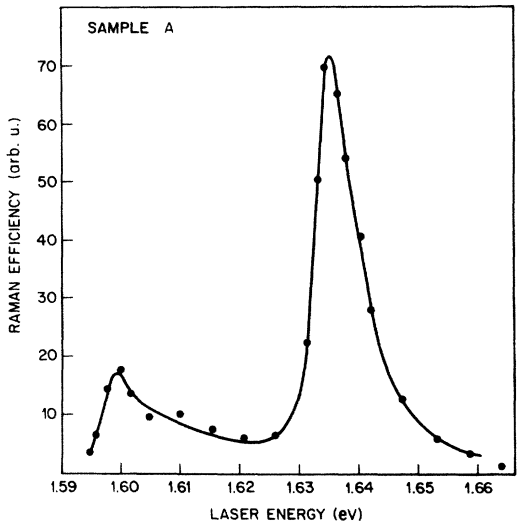

FIG. 3. Resonance of the Raman efficiency for the LO_1 phonon of $Al_xGa_{1-x}As$ in sample A.

gy. The Raman spectra were taken in the polarized configuration, which corresponds to scattering induced by the Fröhlich electron-phonon interaction.[18,25] We see in Fig. 3 an incoming resonance (laser photon energy equal to the excitonic transition) and a better resolved outgoing resonance (scattered photon energy equal to the excitonic transition). From these values and the measured phonon energy [$\hbar\omega(LO_1)=36.25$ meV in our sample] we find an exciton energy of $E_{ex}=1599\pm1$ meV. The actual $Al_xGa_{1-x}As$ band gap can be slightly different from this value, because we have to subtract the difference between the delocalized levels and the barrier heights and add the exciton binding energy. In practice, these two quantities tend to cancel out. The first delocalized level in the conduction band can be calculated to be 2.1 meV above the top of the barrier. For heavy and light hole levels, this quantity is 3.1 and 2.4 meV, respectively (below the valence-band barrier). The total amount, between 4.3 and 5.1 meV, is comparable with the expected binding energy of the delocalized exciton: For $d_1\simeq330$ Å the binding energies of the highest excitons tend to a value slightly below 5 meV (Ref. 26). This should also be valid for the delocalized exciton in our samples with low Al concentration, because the bulk $Al_xGa_{1-x}As$ exciton has a binding energy close to the 4.2 meV estimated for GaAs.[27] We thus conclude that $E_{Al_xGa_{1-x}As}=1599\pm3$ meV gives a safe estimate of the $Al_xGa_{1-x}As$ energy gap.[28] Using the value $E_{GaAs}=1517.7$ meV from Ref. 27, we obtain a total band discontinuity of $\Delta E_g=81\pm3$ meV. This value, together with $\Delta E_c=55.9$ meV, leads to $Q_e=0.69\pm0.03$.

Experiments in other square and parabolic wells[29] confirm this value of Q_e and do not seem to indicate any dependence of Q_e upon the Al concentration x, in agreement with the great deal of experimental data for different values of x (Refs. 3–14). The magnitude of our value for Q_e is somewhat higher than in other optical experiments,[3,12,13] and also higher than the most detailed electrical data available.[8,30] (See Ref. 31 for a critical review of electrical experiments.) However, many of the previous determinations of Q_e are subject to revision because of the experimental difficulties discussed above. As far as the light scattering results are concerned, the main sources of error have been eliminated, so that we consider our value $Q_e=0.69\pm0.03$ to be very accurate.

[1]For reviews, see H. Kroemer, in *Molecular Beam Epitaxy and Heterostructures,* edited by L. L. Chang and K. Ploog (Nijhoff, Dordrecht, 1985); J. Vac. Sci. Technol. B **2**, 433 (1984); G. Duggan, *ibid.* **3**, 1224 (1985).

[2]R. Dingle, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **34**, 1327 (1975).

[3]R. C. Miller, D. A. Kleinman, and A. C. Gossard, Phys. Rev. B **29**, 7085 (1984).

[4]R. C. Miller and D. A. Kleinman, J. Lumin. **30**, 520 (1985).

[5]W. I. Wang, E. E. Méndez, and Frank Stern, Appl. Phys. Lett. **45**, 639 (1984).

[6]W. I. Wang, T. S. Kuan, E. E. Méndez, and L. Esaki, Phys. Rev. B **31**, 6890 (1985).

[7]W. I. Wang and Frank Stern, J. Vac. Sci. Technol. B **3**, 1280 (1985).

[8]M. O. Watanabe *et al.*, J. Appl. Phys. **57**, 5340 (1985).

[9]H. Okumura, S. Misawa, S. Yoshida, and S. Gonda, Appl. Phys. Lett. **46**, 377 (1985).

[10]D. Arnold *et al.*, Appl. Phys. Lett. **45**, 1237 (1984).

[11]J. Batey, S. L. Wright, and D. J. DiMaria, Appl. Phys. Lett. **57**, 484 (1985).

[12]M. H. Meynadier *et al.*, Phys. Rev. B **31**, 5539 (1985).

[13]R. C. Miller, A. C. Gossard, and D. A. Kleinman, Phys. Rev. B **32**, 5443 (1985).

[14]G. Duggan, H. I. Ralph, and K. J. Moore, Phys. Rev. B **32**, 8395 (1985).

[15]W. Pötz, W. Porod, and D. K. Ferry, Phys. Rev. B **32**, 3868 (1985).

[16]A. Pinczuk, J. Shah, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **46**, 1341 (1981).

[17]S. R. White and L. J. Sham, Phys. Rev. Lett. **47**, 879 (1981); A. Fasolino and M. Altarelli, in *Two Dimensional Systems, Heterostructures and Superlattices,* edited by G. Barer, F. Kuchar, and H. Hernwich (Springer, Berlin, 1984), p. 176.

[18]J. E. Zucker, A. Pinczuk, D. S. Chemla, A. C. Gossard, and W. Wiegmann, Phys. Rev. B **29**, 7065 (1984).

[19]U. Rössler, Solid State Commun. **49**, 943 (1984).

[20]A. Pinczuk, H. L. Störmer, R. Dingle, J. Worlock, W. Wiegmann, and A. C. Gossard, Solid State Commun. **32**, 1001 (1979).

[21]G. Abstreiter, M. Cardona, and A. Pinczuk, in *Light Scattering in Solids IV,* edited by M. Cardona and G. Guntherodt (Springer, Berlin, 1984).

[22]Notice that the power densities needed to see the three spectra in Fig. 1 are different: While the transitions E_{01} and E_{02} can be observed for low power densities, higher densities are required for E_{12} and E_{23}, due to the fact that for E_{12}, one needs the quasi-Fermi level to be above the level 1, and for E_{23}, above the level 2.

[23]S. Katayama and T. Ando, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors,* edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1985).

[24]In our sample A, the third excited level is so close to the top of the barrier that small variations of d_1 can affect its energy considerably. This means that for this sample d_1 can be taken as an adjustable parameter. By doing so, one obtains the same value $d_1=335.1$ Å. The remarkable agreement with the TEM value can thus be considered as an additional proof of the accuracy of our light scattering method.

[25]J. E. Zucker, A. Pinczuk, D. S. Chemla, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **57**, 1294 (1983).

[26]J. A. Brum and G. Bastard, J. Phys. C **18**, 89 (1985).

[27]D. E. Aspnes and A. A. Studna, Phys. Rev. B **7**, 4605 (1973).

[28]Using the interpolation formula $E_g(x) = 1.5177 + 1.30x$ (in eV) for the gap of $Al_xGa_{1-x}As$, we deduce for our sample $x = 0.062$. The formula used arises from the known GaAs energy gap at 4 K (Ref. 27), and from the linear coefficient given by Casey and Panish [H. C. Casey, Jr. and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1978)], corrected for low temperatures according to Vorobkalo *et al.* [F. M. Vorobkalo, K. D. Glinchuk, and V. F. Koralenko, Fiz. Tekh. Poluprovodn **9**, 998 (1975) [Sov. Phys. Semicond. **9**, 656 (1975)]]. Incidentally, a very similar linear term ($1.31x$, in eV) has been recently suggested by Kroemer (Ref. 31) from a comparison of band-offset data from different sources.

[29]J. Menéndez, A. Pinczuk, A. C. Gossard, W. Wiegmann, and M. G. Lamont (unpublished).

[30]J. Batey and S. L. Wright, J. Appl. Phys. **59**, 200 (1986). Together with the interpolation formula of Ref. 28, these measurements yield $Q_e \sim 0.58$.

[31]H. Kroemer, in *Proceedings of the Second International Conference on Modulated Semiconductor Structures* [Surf. Sci. (to be published)].