RESONANT SURFACE RAMAN SCATTERING IN DIRECT-GAP SEMICONDUCTORS

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The Raman spectra of optical phonons in InAs, InSb, InP, and GaAs have been studied via reflection techniques, using 5145-, 4965-, 4880-, 4765-, and 4658-Å argon laser excitation. The scattering cross sections in InAs display strong enhancement for laser photon energies near the E_1 saddlepoint gap, and two-phonon processes are observed under these conditions. In InSb the laser frequencies are near the $E_1+\Delta_1$ gap, but no strong enhancement is observed. InP and GaAs were studied far from resonance with any known gap and demonstrate that such gap resonance is not essential for reflection studies of direct-gap semiconductors using visible-spectrum lasers.

Reflection Raman spectroscopy has been used to study small-band-gap semiconductors by Russell[1] (Si), Parker, Feldman, and Ashkin[2] (Ge), Krauzman,[3] and Pinczuk and Burstein[4] (InSb). This technique is easier for indirect-gap materials like Si than for the direct-gap III-V semiconductors, because the larger absorption coefficients in the latter produce much smaller scattering volumes. In the case of InSb, Pinczuk and Burstein attributed their large cross sections and anomalous LO/TO intensity ratios at different temperatures to a resonance of the incident photon energy with the E_1 interband gap. While the He-Ne laser frequency is relatively near that of E_1 gap in InSb, that laser is operative at only a single frequency, and direct verification of the inferred E_1 resonance by varying the laser frequency is not possible. Consequently, in the present experiment we have examined reflection Raman scattering in InAs, whose E_1 gap is at approximately 2.5 eV,[5] using argon ion lasers operating at ~2.40, 2.50, 2.55, 2.60, and 2.65 eV. We have found that the Raman cross section exhibits a maximum near the E_1 gap and that two-phonon scattering is observable only when near resonance (i.e., at 4765 Å in InAs). The two-phonon processes occur at almost exactly twice the frequencies of the one-phonon zone-center features and have also been seen in CdS near resonance.[6,7] We believe that they are a phenomenon characteristic of direct-gap resonances.

Scattering from [111] surfaces in InAs was examined with incident light at 10 to 40° angles. Near-normal incidence was avoided in order to eliminate specularly reflected light from the collection optics. Both Stokes and anti-Stokes lines were recorded. The observed data show neither dependence upon the angle of incidence nor on the angle between the polarization of the incident beam and the plane of the observing surface. This is presumably a consequence of refraction and demonstrates that we may consider all incident geometries used to be nominally equivalent to propagation along [111] normal to the observing surface and polarization in the surface plane. Both diagonal and nondiagonal scattering were observed. That is, $z(xx)z$ and $z(xy)z$ geometries were employed. The shorthand notation $z(xy)z$ designates incident and scattered photons polarized, respectively, along x and y and propagating along z. In our InAs experiments we had $x=[1\bar{1}0]$, $z=[111]$, and $y=[11\bar{2}]$.

It can be shown that for the [111] direction of propagation considered here, TO phonons produce both xx and xy scattering while LO phonons produce only xx scattering. This is consistent with the InAs data shown in Fig. 1. The weak LO scattering for α_{xy} polarization is presumably induced by the surface electric field, as proposed by Pinczuk and Burstein in the case of InSb,[4] rather than incomplete polarization discrimination, since it remained unaffected by changes in scattering angle and solid angle of the collection optics. The effects of electric fields on surface Raman scattering in InAs have been examined in some detail by Nill and Mooradian,[8] and will not be discussed here. None of our measurements on InAs was chosen to illustrate surface field effects, which are best demonstrated at low temperatures with [110] faces (where the LO-phonon scattering is completely field induced).

We have, however, investigated several other III-V semiconductors. Scattering from [110] faces of InSb, GaAs, and InP was carried out as a comparison with the InAs behavior. None of these materials exhibited a significant dependence of Raman cross section upon argon laser frequency. In particular, no enhancement was observed for 5145-Å excitation, although this wavelength is very near that of the $E_1+\Delta_1$ spin-

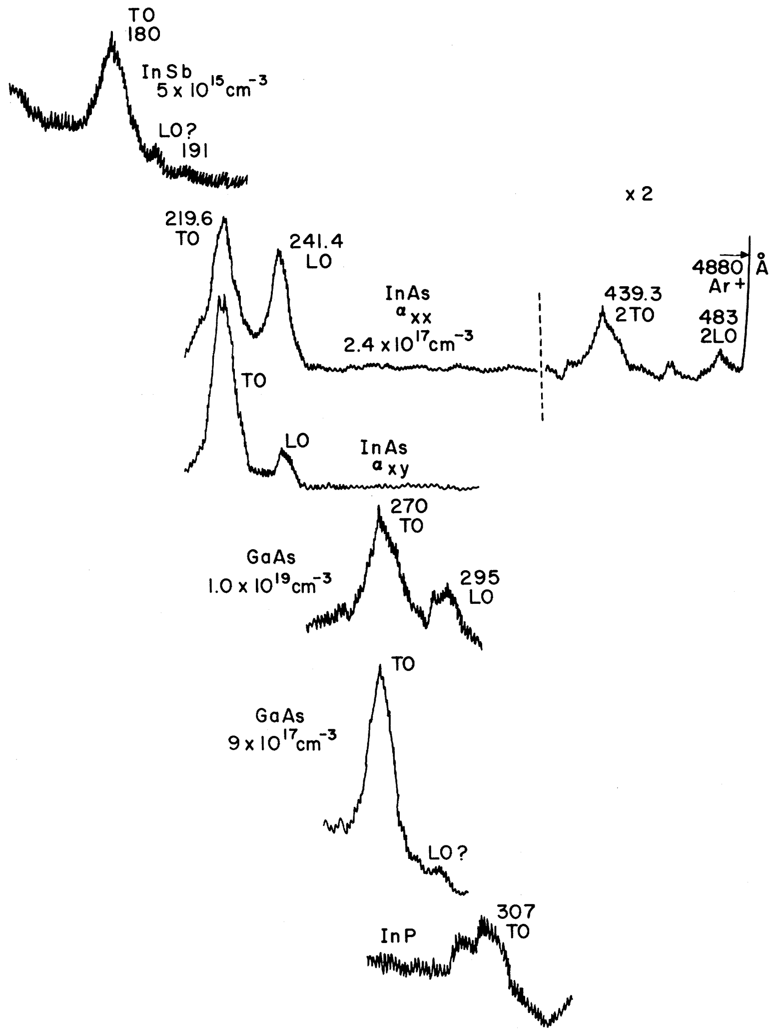

FIG. 1. Representative data at 300°K for InAs, InSb, GaAs, and InP samples. The InAs data shown are for [111] faces; the others are [110]. Scattering intensities are plotted versus frequency shift in cm^{-1} from the 4765-Å laser source.

orbit-split interband transition in InSb. We also observed no surface electric-field-induced LO-phonon scattering in InSb near $E_1+\Delta_1$. According to the theory of Pinczuk and Burstein[4] this is presumably because of the low carrier concentration (bulk) of our sample: 5×10^{15} cm^{-1}.

While the absolute cross sections in GaAs were very large, no two-phonon processes were observed. This is compatible with the band structure of GaAs,[9] which shows no interband gap near the laser frequencies used. This suggests that while direct-gap resonance is required for observable scattering from multiphonon $K\approx 0$ processes, no such gap resonance is necessary for strong first-order reflection scattering above the band gap. The GaAs and InP spectra in Fig. 1 demonstrate this. Note the "forbidden" LO-phonon scattering in the GaAs sample containing 10^{19} carriers/cm^3.

It is important to realize that for a carrier concentration of 2.4×10^{17} cm^{-3}, InAs should manifest a strongly coupled plasmon-LO-phonon excitation whose frequencies differ substantially from the LO frequency in pure InAs. This is completely inconsistent with our data, which show an LO phonon at 241.4 cm^{-1}, almost exactly where it has been assigned from emittance measurements.[10] This indicates that all of our scattering occurred in a carrier-free depletion layer, as proposed by Pinczuk and Burstein. This is also true of the GaAs scattering, and shows that the depletion layer scattering will be observed independent of any gap resonance.

Figure 2 shows the InAs cross-section depen-

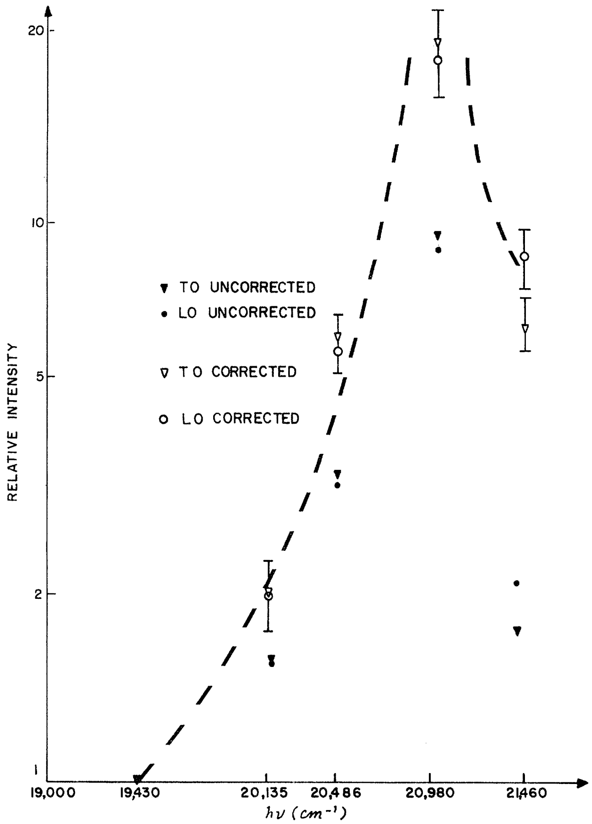

FIG. 2. Scattering cross sections in InAs (arbitrary units) as a function of laser frequency. The data were obtained with 40 mW in each line and have been corrected for frequency dependent absorption and the ν^4 law. The largest correction (for 4658 Å) was of the order of ×3.

dence upon the frequency of the incident radiation. Correction due to absorption was made by using Cardona's absorption data[5] together with Loudon's correction formula.[11] The shape of the resonance curve in Fig. 2 is, however, quite different from that obtained in CdS and ZnSe,[6] where the results for the LO phonon were accounted for by means of the theory developed by Ganguly and Birman.[12] One should not expect the above theory to be valid here since the E_1 exciton is at a saddle point. No theory for resonance Raman effect at saddle points is available presently. In contrast with what was inferred in InSb,[4] the dependence upon laser frequency of the intensities of LO- and TO-shifted Raman lines are almost exactly the same in InAs, as shown in Fig. 2. Note that the LO intensities plotted here are "allowed" and not field induced; thus direct comparison with data of Pinczuk and Burstein or Nill and Mooradian is not possible.

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[1]J. P. Russell, Appl. Phys. Letters 6, 223 (1965).

[2]J. H. Parker, Jr., D. W. Feldman, and M. Ashkin, Phys. Rev. 155, 712 (1967).

[3]M. Krauzman, Compt. Rend. 264B, 1117 (1967).

[4]A. Pinczuk and E. Burstein, Phys. Rev. Letters 21, 1073 (1968), and in Proceedings of the International Conference on Light Scattering Spectra of Solids, edited by G. B. Wright (Springer-Verlag, Berlin, Germany, to be published).

[5]M. Cardona and G. Harbeke, J. Appl. Phys. 34, 813 (1963).

[6]R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters 17, 10 (1966).

[7]R. C. C. Leite, T. C. Damen, J. F. Scott, in Proceedings of the International Conference on Light Scattering Spectra of Solids, edited by G. B. Wright (Springer-Verlag, Berlin, Germany, to be published).

[8]K. Nill and A. Mooradian, Bull. Am. Phys. Soc. 13, 1658 (1968).

[9]M. Cardona, K. Shaklee, and F. Pollak, Phys. Rev. 154, 696 (1967).

[10]D. L. Stierwalt and R. F. Potter, in Semiconductors and Semimetals, edited by R. K. Willardson and A. C. Beer (Academic Press, Inc., New York, 1967), Vol. 3, p. 87.

[11]R. Loudon, J. Phys. (Paris) 26, 677 (1965).

[12]A. K. Ganguly and J. L. Birman, Phys. Rev. 162, 806 (1967).