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RAMAN SCATTERING FROM InSb SURFACES AT PHOTON ENERGIES NEAR THE E_1 ENERGY GAP*

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(Received 3 September 1968)

We have observed surface electric-field–induced and resonance-enhanced Raman scattering by $q \approx 0$ LO phonons in the spectra obtained from InSb surfaces. The data indicate that excitons are responsible for the resonance enhancement. The effects of temperature and externally applied electric fields are discussed. The results suggest the possibility of studying the surface electronic properties by Raman spectroscopy.

During a series of experiments performed to obtain the Raman scattering spectra of coupled LO-phonon–plasmon modes in n-type InSb using a He-Ne laser at 6328 Å and a backward scattering geometry, we found that the $q \approx 0$ LO phonon appears at a frequency $\omega_{LO} = 191$ cm^{-1} regardless of the concentration of carriers in the volume of the crystal. Further, the $q \approx 0$ LO-phonon band is observed for scattering geometries in which, according to the polarization selection rules for the Raman scattering tensor (RST),[1] it should be forbidden. The strengths of the $q \approx 0$ LO-phonon band in these scattering geometries were, however, observed to increase with increasing conduction-electron concentration. It is shown in this Letter that these effects are due to the depletion layer at InSb surfaces[2] whose thickness is comparable with or larger than the skin depth at 6328 Å. This accounts for the observed independence of the LO-phonon frequency on the carrier concentration in the volume of the crystal. The breakdown of the selection rules for the first-order RST and the increasing strength of the $q \approx 0$ LO-phonon band with increasing carrier concentration in the volume of the crystal are attributed to an electric-field–induced Raman scattering by the electric field present in the depletion layer. In addition, the large observed scattering intensities and their temperature dependence indicate a resonance effect which, unlike previous observations of resonant Raman scattering at the fundamental energy gap,[3] occurs at the E_1 energy gap (1.89 eV).[4]

The experiments were performed on undoped and Te-doped InSb crystals of n type with carrier concentrations in the range from 1.5×10^{15} to 1.4×10^{18}/cm^3.[5] (110) surfaces were obtained by cleavage in air and no further treatment was given to the surface. The spectra were excited with a 50-mW He-Ne laser operating at 6328 Å (1.96 eV). In order to identify the spectra, the (110) surface is described by the following Cartesian system of coordinates: $y \equiv [110]$, which is normal to the surface, and $x' \equiv [1\bar{1}1]$ and $z' \equiv [\bar{1}12]$, which are contained in the surface.

The spectra of Fig. 1, showing the $q \equiv 0$ TO- and LO-phonon bands, correspond to the $(x'x')$ component of the RST. The incident and scattered radiation (inside the crystal) as well as the scattering wave vector $\vec{q} = \vec{k}_{inc} - \vec{k}_{scatt}$ were along y'. Similar spectra were obtained for the $(z'z')$ component, while the spectra for the $(z'x')$ component show only the band of the $q \approx 0$ TO phonons. According to the selection rules for the first-order RST,[1] the $q \approx 0$ LO-phonon band is forbidden for the scattering geometries and the polarizations of the incident and scattered radiation corresponding to the three types of spectra.

Due to the large absorption coefficient of InSb at 6328 Å, the observed scattered radiation originates only from the skin depth, which is about 500 Å. Since no changes are observed in the $q \approx 0$ LO-phonon frequency, we have to assume that the concentration of carriers in this region is smaller than 1×10^{15}/cm^3.[6] This indicates the presence of a depletion layer with a width which is at least of the same order as the skin depth. It has been shown[2] that the Fermi level at InSb surfaces is pinned at a fixed position within the forbidden energy gap which is independent of the doping of the material and of temperature in the range between 300 and 77°K. Under these condi-

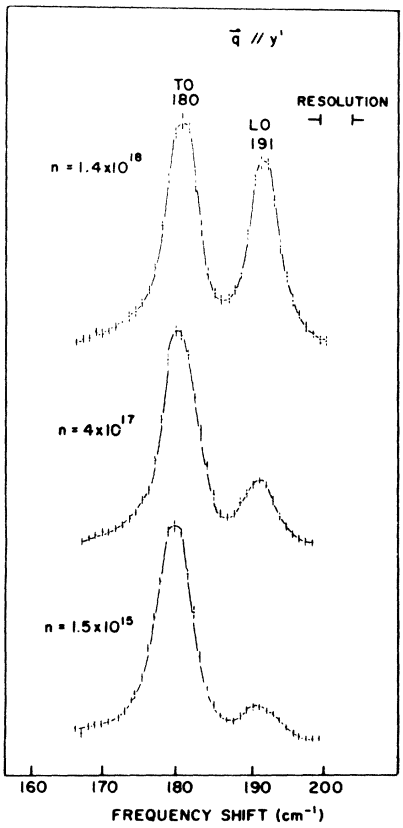

FIG. 1. Spectra of the $(x'x')$ component of the RST of InSb samples with different carrier concentrations n in the volume. The bands of the $q \approx 0$ TO and LO phonons are shown.

tions, the electric fields in the depletion layer are of the order of 10^5 V/cm and increase with increasing carrier concentration in the volume of the crystal. This results from the rise in the Fermi level in the bulk of the sample and from the charge built up in the surface states in order to pin the Fermi level at the surface at a fixed position in the forbidden energy gap. The width of the depletion layer decreases with increasing carrier concentration in the volume; for the sample with $n = 1.4 \times 10^{18}/\text{cm}^3$ it is estimated to be about equal to the skin depth at 6328 Å.

It seems natural to attribute our results to the lowering of the crystal symmetry at the surface by this electric field (surface-electric-field-induced Raman scattering). An electric-field-induced Raman scattering has been observed in paraelectric crystals[7] and in diamond[8] with electric fields applied externally to the volume of the samples. This is the first time that such an effect is reported for surface electric fields. The nonzero components of the RST corresponding to the electric-field-induced effect to any order in the electric field strength can be found using the phenomenological theory of the electric-field-induced Raman scattering.[9] In agreement with our spectra, it is found that to the first nonvanishing order in the field strength (the Raman cross section will go as the square of the field), no surface-field-induced scattering is expected on the $q \approx 0$ TO phonon independent of crystal orientations and polarizations of the incident and scattered radiation. On the other hand, for the scattering geometry of the spectra reported here, a surface-field-induced $q \approx 0$ LO-phonon band is expected in the spectra of the $(x'x')$, $(z'z')$, $(x'z')$, and $(z'x')$ components of the RST. As reported above, the $q \approx 0$ LO-phonon band does appear in the $(x'x')$ and $(z'z')$ spectra but it is absent in the $(x'z')$ and $(z'x')$ spectra. On the basis of the theory of Burstein and co-workers[9] it can be shown that unless an accidental cancellation of terms occurs, this result can be explained only if the diagonal components of the RST for electric fields parallel to the phonon displacement dominate the spectra, when the scattering geometry is such that the electric fields, phonon displacements, and photon polarization are along [100] axis. The microscopic basis for this result is not yet clear. It may be related to the mechanism of the resonance enhancement which would be sensitive, for example, to the symmetry properties of the electronic energy bands at the E_1 energy gap.

Figure 2 illustrates the effects of temperature changes. On decreasing the temperature from 296 to 140°K, the intensity of the $q \approx 0$ LO-phonon band increases by a factor of about 6, while no changes are found in the intensity of the $q \approx 0$ TO-phonon band. Since no dramatic changes are expected in the surface electric field in this temperature range, the increase in the intensity of $q \approx 0$ LO-phonon cannot be explained by surface effects. However, we note that the spectra are obtained in the regime of resonant scattering since the laser radiation used to produce the spectra has an energy (1.96 eV) which is very close to the E_1 energy gap at 1.89 eV ($T = 300$°K).[4] Resonance-enhanced Raman scattering can occur with free-electron–hole pairs and excitons[10] as intermediate states. Since a similar enhancement would be expected for the TO- and LO-phonon bands if the resonance mechanism involves free-electron–hole pairs, the absence of changes in the intensity of the TO-phonon band with decreasing temperature strongly suggests that excitons

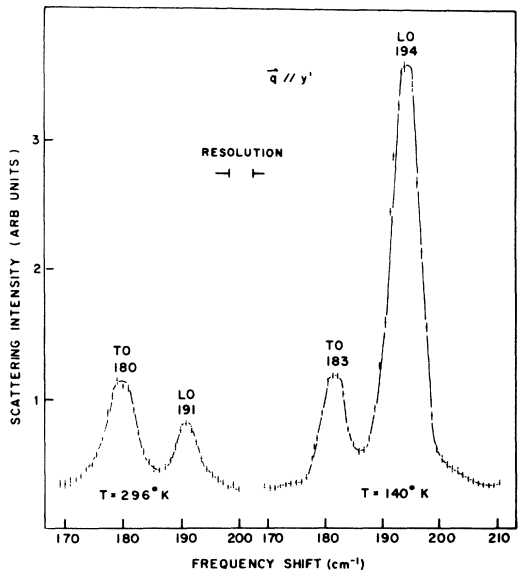

FIG. 2. Temperature dependence of the spectra of the $(x'x')$ component of the RST of an InSb sample with $n = 1.4 \times 10^{18}$.

are responsible for the observed resonance enhancement of the field-induced scattering by the LO phonon. This follows from the fact that the interaction between excitons and TO phonons is weak. Evidence for exciton behavior at the E_1 energy gap of InSb has been given by Cardona and Harbeke.[4] On decreasing the temperature of the sample, two effects occur: The E_1 energy gap moves closer to the energy of the laser photons and the lifetime of the exciton corresponding to the E_1 energy gap increases. As discussed by Burstein et al.,[11] who give a theory of the electro-optic contributions to exciton-enhanced Raman scattering, both effects result in an increase of the exciton strength at the energy of the laser photons and thereby in an increase in the exciton-enhanced scattering efficiency of the LO phonons.

We have also carried out experiments in which an external dc electric field was applied to the (110) surface of InSb using a technique described by Cardona, Shaklee, and Pollak.[12] When the sample was biased negatively so that the barrier height and the electric field in the depletion layer are reduced, a large reduction in the intensity of the $q \approx 0$ LO-phonon band is found for bias voltages greater than 1.8 V. This is in agreement with the hypothesis of a surface-electric-field-induced Raman scattering.

Finally, we would also like to point out that our results establish the possibility of studying the surface electronic properties of small-gap semiconductors by Raman spectroscopy.

We would like to acknowledge stimulating discussions with J. Zemel and D. L. Mills.

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*Work supported by the U. S. Army Research Office, Durham, North Carolina.

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