It probably cannot be determined at this point whether or not the extrapolation to KCl is valid, or if in fact the RES wave function is somewhat different for KCl.

A few years ago it was generally thought that detection of ESR and ENDOR in the RES of the F center would be impossible. Yet the experiments have now been done, and interpretation of the ENDOR has proven remarkably straightforward and rather definitive. We trust that this work will form a solid cornerstone for further theoretical work on the RES. In particular, we would urge a refinement of the relaxation calculations, and an extension of Ham's treatment to include the ESR g factor and other magnetic effects.

Note added.—Following completion of this manuscript, we succeeded in detecting ENDOR of the RES in KBr for the first time. As expected, the spectrum is not resolved, but a value of $(\nu_{hf})_{max} = 11.8 \pm 0.5$ MHz for Br^{81} can be extracted from it. Again, assuming a pure $|2p\rangle$ state, and analyzing as above, we obtain $\eta \sim 0.48$ in KBr and $A \sim 3000$ for Br.

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Resonance Raman Scattering in InSb near the E_1 Transition*

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Resonance Raman scattering in InSb near the E_1 transition has been measured at low temperatures for various different configurations with a tunable dye laser. The experimental curves show a resonance peak at an incident photon energy appreciably higher than the energy of the E_1 peak in the reflectivity spectra, contrary to the predictions of existing theories. Double resonance in the Raman tensor involving transitions in the band continuum is proposed to explain the result.

Recently, considerable theoretical[1] and experimental[2-5] interest has been focused on resonance Raman scattering (RRS). However, most of the experimental investigations have so far been carried out with only a few discrete laser frequencies. Since these discrete laser frequencies are separated by 0.1 eV or more, it becomes difficult to obtain detailed information about RRS, especially for resonances which have half-widths smaller than 0.1 eV. This difficulty is overcome with the availability of tunable dye lasers.[6] Measurements of RRS using a tunable dye laser have already been reported in CdS near bound exciton lines[7] and in Ge near the E_1 and $E_1 + \Delta_1$ transitions.[8] This Letter is a preliminary report of a detailed study of RRS by TO and LO phonons in InSb near the E_1 transition carried out with a cw tunable dye laser. Our results indicate that in InSb the E_1 hyperbolic exciton contributes negligibly to the RRS, but rather, it is transitions involving the band continuum that are responsible for the observed resonance enhancement in the

Raman scattering of the TO and LO phonons. This is contrary to what Pinczuk and Burstein proposed to explain their results on the surface-field-induced Raman scattering in InSb.[2]

The samples used in our measurements were all n type with carrier concentrations between 10^{14} to 10^{15} cm^{-3}. The sample surfaces were prepared either by cleaving ([110] face) or by mechanical polishing followed by etching ([100] and [111] surfaces). After surface preparation, the sample (thickness $\lesssim 0.5$ mm) was placed on the cold finger of an optical Dewar with a vacuum better than 10^{-5} Torr. The optical setup was typical of a Raman spectrometer using photon-counting techniques. A cw dye laser (Spectra model 70) tunable from 1.98 to 2.16 eV was used as the exciting source. The integrated intensity of the scattered light was normalized against the intensity of the 283-cm^{-1} line of calcite measured under similar conditions.

The following scattering configurations have been studied: (a) $Z(XX)Z$, (b) $Z(YX)Z$, (c) $Z'(X'X')Z'$, (d) $Z'(Y'X')Z'$, (e) $X'(Y'Y')X'$, and (f) $X'(Z'Y')X'$, where X, Y, Z, and X', Y', Z' respectively denote the [100], [010], [001], and [1$\bar{1}$1], [1$\bar{1}\bar{2}$], [110] directions. These configurations have been chosen to correspond to different physical situations. Assuming that the wave vector q of the incident photon is negligible, one can show that in case (a) Raman scattering by both the LO phonon (LOR) and the TO phonons (TOR) is forbidden, but the surface-electric-field-induced Raman scattering by the LO phonon (SFR) is allowed. In case (b), LOR is allowed while TOR and SFR are forbidden. In cases (c) and (d), LOR is forbidden but TOR and SFR are allowed. In case (e), all three processes are allowed. Finally, in case (f), only TOR is allowed. In all cases, the effect of surface field on TOR has been assumed to be negligible. We found in our experiments that the above selection rules were obeyed and that SFR was negligible if the incident laser frequency ω_l was far away from the E_1 peak.

Figure 1 shows the measured scattering cross section as a function of ω_l near the E_1 transition for LOR in case (b), SFR in case (c), and TOR in case (f). No correction due to dispersion in the absorption coefficient of the sample was necessary since it is negligible over the small energy range of our measurement. We notice that the shapes of the LOR and the TOR curves in Fig. 1 are similar, but are quite different from that of the SFR curve, the latter being appreciably sharper. Both the LOR and the TOR have a maximum

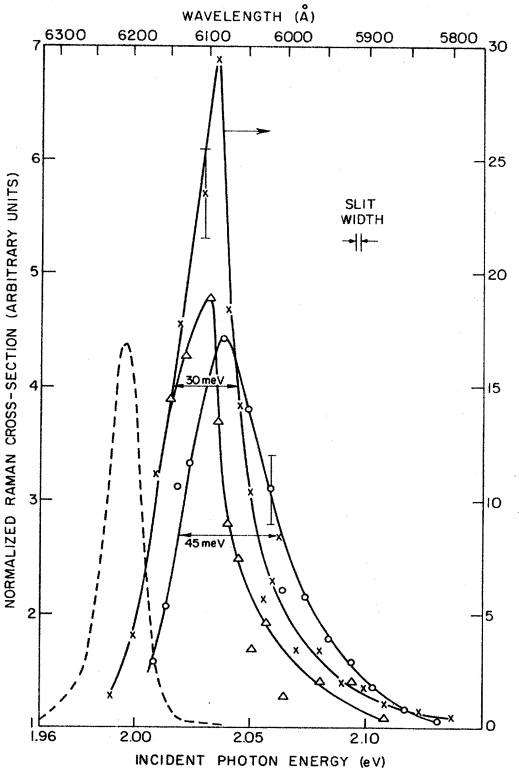

FIG. 1. Experimental Raman scattering cross section of InSb as a function of incident photon frequency. Crosses, SFR of the LO phonon in case (c) ($T = 12$°K). Triangles, LOR in case (b) ($T = 14$°K), and circles, TOR in case (f) ($T = 10$°K) (see text). Dashed curve, $|d\chi/d\omega|^2$ obtained from the experimental wavelength-modulated reflectivity spectrum of InSb ($T = 5$°K) in Ref. 7.

resonance enhancement of approximately a factor of 4, while the SFR has a maximum enhancement of more than 60. These suggest that the resonance enhancement of the LOR and the TOR is probably due to the same mechanism which is different from that of SFR. The TOR curves measured in the other cases all have essentially the same shape as the TOR curve in Fig. 1, indicating that surface field has negligible effect on TOR.

A comparison of the resonance enhancement of SFR in case (a) (Fig. 1) and LOR + SFR in case (e) (Fig. 2) shows that in case (e), near the resonance peak, Raman scattering by LO phonons is predominantly due to SFR. Furthermore, absolute intensity measurements in the two cases show that there is constructive interference between the Raman tensor of LOR and SFR.

The most surprising feature of the resonance enhancement curves in Fig. 1 is that in all three

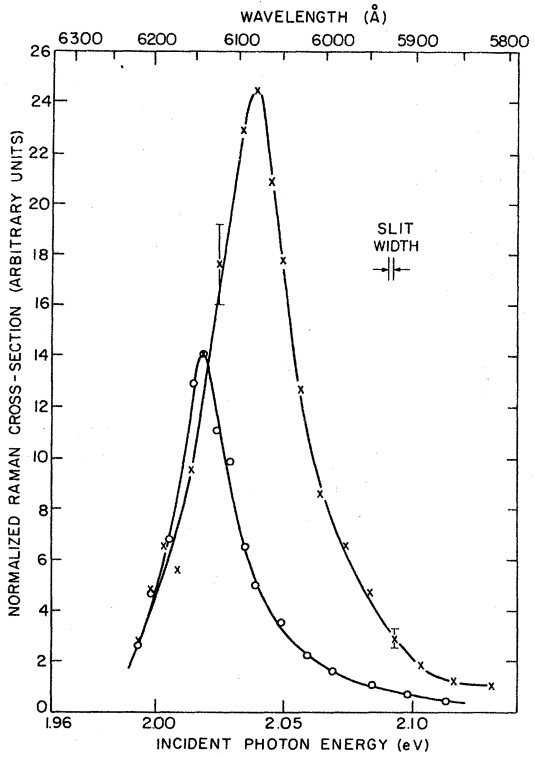

FIG. 2. Cross section of the surface-field–induced Raman scattering by LO phonons [case (e)] at 10°K (crosses) and 83°K (circles).

cases the peak occurs at incident photon energies around 2.035 eV, whereas the E_1 peak in the reflectivity spectrum of InSb at 5°K occurs at 1.983 eV.[9] Similar results have been observed earlier by others in InAs, Ge, and Ge-Si alloys.[3,4,8] It is now well established that excitonic effects play an important role in the optical spectra of InSb at the E_1 peak.[10] If this were also true in RRS, existing theories[1] would predict two peaks in the resonance enhancement curve, one at 1.983 eV and the other at 2.005 eV (corresponding to scattered photon energy $\hbar\omega_s = 1.983$ eV). The two peaks may overlap and appear as a single peak occurring between 1.983 and 2.005 eV.[1,8] Our results therefore suggest that transitions involving band continuum are probably more important in the present case. Let us write the Raman tensor as[2]

$$R = \frac{\partial\chi(E_s)}{\partial u} + \frac{\partial\chi(E_s)}{\partial E}\frac{\partial E}{\partial u}, \qquad (1)$$

where $\chi(E_s)$ is the electronic susceptibility at ω_i under the influence of the surface electric field E_s, and E is the infrared macroscopic electric field associated with the lattice vibration u. The first term in Eq. (1) is due to electron-phonon interaction via the deformation potential, and the second term is due to the Fröhlich interaction.[11] For TO phonons, $\partial E/\partial u = 0$. Our experimental results suggest that $\partial\chi(E_s)/\partial u \simeq \partial\chi(0)/\partial u$, and that the Fröhlich term in Eq. (1) is responsible for SFR. With no surface field, the Fröhlich term is small since the intraband Fröhlich interaction is zero.[11] But with a surface field, the intraband Fröhlich interaction can be nonzero and, in our case, SFR appears dominant over TOR and LOR near the resonance peak.

It has been pointed out that within a two-band model $\partial\chi/\partial u \propto \partial\chi/\partial\omega_i$ near resonance in the limit of zero phonon frequency.[2] This two-band approximation is valid in case of InSb at E_1 where the spin-orbit splitting is large.[8] We notice that $\partial\chi/\partial\omega_i$ is related to the wavelength-modulated reflectance of the sample. On the other hand, the Fröhlich interaction term $\partial\chi(E_s)/\partial E$ is related to the electroeflectance of the sample (biased at E_s). From the electroeflectance[12] and wavelength-modulated reflectance[9] of InSb, we can conclude that the E_1 peak in $\partial\chi/\partial u$ and $\partial\chi/\partial E$ should appear at the same energy, but $\partial\chi/\partial E$ should be sharper than $\partial\chi/\partial u$ because of the Franz-Keldysh effect.[13] This explains qualitatively why the curve of SFR is sharper than those of TOR and LOR in Fig. 1.

We have plotted in Fig. 1 the dispersion of $|\partial\chi/\partial\omega_i|^2$ which has the exciton-enhanced E_1 peak at 1.996 eV. This peak is about 40 meV below the peaks in the RRS curves in Fig. 1. We can therefore conclude that the E_1 hyperbolic excitons do not play an important role in RRS of InSb. This is contrary to what Pinczuk and Burstein concluded from their measurements on the temperature dependence of SFR.[2]

Cerdeira, Dreybodt, and Cardona[8] have shown that when the spin-orbit splitting Δ_1 at E_1 is small, as in the cases of Ge and InAs, this shift of the Raman resonance peak can be explained, at least in part, by the overlapping resonant contributions from the E_1 and the $E_1+\Delta_1$ peaks. However, they have also pointed out that in compounds with large Δ_1 such as GaSb and InSb, this overlapping effect is negligible and the two-band approximation we mentioned above is valid. This is particularly true at low temperatures where the exciton peaks become much sharper. The observed shift of the Raman resonance in InSb must therefore arise from a different origin.

We have attempted to explain this difference of ~40 meV in InSb as due to the binding energy of the E_1 hyperbolic exciton. However, Kane's mod-

el[14] of hyperbolic excitons predicts a binding energy of only 11 meV for the E_1 exciton of InSb. To account for the remaining ~30 meV, we propose the following explanation: The energy denominator of the most dispersive term in the microscopic expression of the Raman tensor obtained by Loudon[11] can be written as

$$[\omega_c(\vec{k}+\vec{q}_l)-\omega_v(\vec{k})-\omega_l] \times[\omega_c(\vec{k}+\vec{q}_s)-\omega_v(\vec{k})-\omega_s], \quad (2)$$

or

$$[\omega_c(\vec{k})-\omega_v(\vec{k}-\vec{q}_l)-\omega_l] \times[\omega_c(\vec{k})-\omega_v(\vec{k}-\vec{q}_s)-\omega_s], \quad (2')$$

where $\vec{q}_l$ and $\vec{q}_s$ are the wave vectors of the incident and scattered photons, respectively, and $\hbar\omega_c(k)$ and $\hbar\omega_v(k)$ are the energies of electronic states with wave vector $\vec{k}$ in the conduction and valence bands, respectively. Assume that $q=|\vec{q}_l| \simeq|\vec{q}_s|$. For a back-scattering geometry $\vec{q}_l=-\vec{q}_s$, the expressions (2) and (2′) become equivalent. So far, most theories on RRS have assumed that $q\simeq 0$ and predicted that resonances will occur when one of the two terms in (2) or (2′) becomes zero. This implies that if ω_g is the energy of the E_1 peak, resonances will occur at $\omega_l=\omega_g$ or $\omega_s=\omega_g$. We propose, however, that the strongest resonance should occur when both terms in the expressions (2) or (2′) with $q\neq 0$ vanish. We can assume that the valence-band and conduction-band masses in the [111] direction are essentially infinite. Then, the condition for double resonance in the Raman tensor can be written

$$\omega_g+\frac{(\vec{k}_\perp+\vec{q}_\perp)^2}{2\mu_\perp}=\omega_l, \quad \omega_g+\frac{(\vec{k}_\perp-\vec{q}_\perp)^2}{2\mu_\perp}=\omega_s, \quad (3)$$

where $\vec{k}_\perp$ and $\vec{q}_\perp$ are, respectively, the projections of $\vec{k}$ and $\vec{q}_l$ onto the plane perpendicular to the [111] axis, and $\mu_\perp$ is the transverse reduced mass of the valence and conduction bands along [111]. It can be shown that Eq. (3) can be satisfied for $\omega_l\geq\omega_m$ where ω_m is given by

$$\omega_m=\omega_g+\frac{(\omega_0+2q_\perp^2/\mu_\perp)^2}{8q_\perp^2/\mu_\perp}, \quad (4)$$

where ω_0 is the phonon frequency. Also, the density of states satisfying (3) has the form $N(\omega) \propto(\omega-\omega_m)^{-1/2}$ for $\omega\geq\omega_m$.[15] The resonance enhancement should then occur at ω_m instead of ω_g. Broadening is expected to remove the infinity singularity at ω_m. Using the values $\hbar\omega_0=22$ meV, $\mu_\perp=(1/19.7)\times$(mass of free electron,[16] and $|q_\perp| \simeq 4.4\times10^5$ cm^{-1}, we obtain $\omega_m-\omega_g=33$ meV. This, in addition to the estimated binding energy of the exciton, is in good agreement with the observed shift of ~40 meV. It should be noted that our model predicts only one resonance peak as opposed to the two peaks predicted by existing theories,[1] which assume $q\simeq 0$. The model also predicts that the resonance peak should shift with scattering geometry. For the configurations we have studied, the shift is too small to provide a valid test of the model.

We have also studied the temperature dependence of RRS in InSb between 10 and 83°K. We found that the peaks in the resonant enhancement curves shift together towards lower energies with an increase in temperature. The scattering intensities of TOR and LOR varied little between 10 and 83°K, while the corresponding change in SFR was more appreciable. Figure 2 shows the resonance enhancement of SFR measured at 10 and 83°K. The resonance peaks shift by 20 ± 5 meV between 10 and 83°K as compared to 31 meV for the E_1 peak in the reflectivity spectra of InSb.[7] The difference can probably be explained within our model as due to a change in the transverse mass $\mu_\perp$ with temperature. The strong temperature dependence of SFR in InSb led Pinczuk and Burstein[2] to conclude that the hyperbolic exciton at E_1 is responsible for SFR. Since we have already shown that excitonic effects should not be important for SFR in InSb, the observed decrease in the peak scattering intensity with increase in temperature must be caused by a decrease in the surface field or in the matrix elements of the Fröhlich interaction. Further investigations with the surface field carefully monitored are necessary in order to clarify this problem.

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Localized States in Amorphous Tellurium

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We report the observation of strong nonmonotonic behavior in the photoemission quantum yield of vapor-deposited, amorphous Te films and attribute it to emission from localized states about the bottom of the *d* conduction band. A theoretical model is proposed which indicates that the observed yield behavior is due to a mobility edge associated with a relatively high proportion of chain-end imperfections which give rise to well-defined localized states in these films.

The localized or extended nature of electron states in amorphous semiconductors, especially those which are located near the former band edges of the crystal, is a controversial question. Theoretical treatments[1-3] have shown that structural disorder can lead to a smearing out of the sharp band edges with the appearance of an exponential "tail" of localized states which extend above and below the band. States which lie deep within the bands remain delocalized. A rather sharp demarcation between the localized and extended states is indicated by electrical transport studies,[4,5] which define a mobility gap of approximately the same magnitude as the crystalline forbidden band gap. The localized states in the exponential tails are in general associated with random disorder rather than with individual imperfections.[6] It has been postulated, however, that in some covalently bonded amorphous semiconductors, the short-range order is so well preserved that specific structural defects may recur, e.g., nonbridging atoms, chain ends, etc., which would have well-defined energy levels associated with them.[7] These would be expected to give rise to peaks or nonmonotonic behavior in the density of states near the band edge.[7] However, there has been little direct optical or photoemission evidence to support the various theoretical models in view of the apparent low density of localized states in the forbidden band gap of materials studied to date.[8,9] In this Letter, we report the observation of strong nonmonotonic behavior in the photoemission quantum yield of vapor-deposited, amorphous Te films, which is attributed to emission from localized states situated below the bottom of the second (*d*-like) conduction band. Photoemission from these localized states is directly observable in the energy distribution curves (EDC's). A simple theoretical model is proposed in order to explain features of the yield data, and indicates that the observed yield behavior is due to a concentration of such states associated with a relatively high proportion of chain-end imperfections in these films.

Films of thickness of order of 1000 Å were