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Electron-Phonon Interactions in InSb Junctions

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Both oxide-coated and vacuum-cleaved InSb tunnel junctions have been prepared from single-crystal material with 7×10^{13} carriers/cm^3. Capacitance measurements at 4.2 °K show that the barrier height is approximately the same as the energy gap at that temperature. The differential conductance of the junctions as a function of bias voltage shows at least 30 oscillations with a periodicity equal to the LO phonon energy. These oscillations show a striking resemblance to the oscillatory photoconductivity spectra observed in single-crystal InSb and, in fact, a satisfactory model proposed for the tunnel junctions involves a bulk conductance which changes in an oscillatory fashion due to the same mechanism as in the photoconductivity effect. Structure due to both the LA and TA phonons are observed near zero bias owing to inelastic tunneling processes. Further structure, which is particularly prominent in the vacuum-cleaved junctions, is interpreted as the transfer of carriers into the upper L_1 band and this gives an energy of 0.39 ± 0.01 eV between the conduction-band minima of L_1 and Γ_1 at the center of the zone.

I. INTRODUCTION

The first InSb tunnel diodes were made by Batdorf *et al.*[1] and a negative-resistance region (the Esaki characteristic) was observed between 78 and 273 °K. Chynoweth, Logan, and Wolff[2,3] have studied the magnetic field and temperature dependence of the tunneling in similarly prepared InSb *p-n* junctions. The observation of LO phonon interaction was first reported by Hall *et al.*[4–6] for III-V compound *p-n* tunnel junctions studied at 4.2 °K. A measurement of the derivative of the current, dI/dV, vs the voltage V for InSb showed structure when a phonon-assisted tunneling threshold of 24 meV was reached. Hall *et al.*[4] also reported the observation of a conductance minimum at zero bias and interpreted this as polaron formation. They ruled out the possibility that the conductance minimum was associated with acoustic phonon emission by temperature measurements of the tunnel current. However, this possibility has been reconsidered in a calculation by Bennett *et al.*[7] who have shown that such structure can result from TA phonon interactions which allow inelastic tunneling.

A theory of polar-phonon-assisted tunneling has been proposed by Dumke *et al.*,[8] who have considered the case of a direct phonon-assisted component of the current. It is emphasized that this is quite a different problem from the phonon-assisted indirect transitions which must be considered for indirect-gap materials such as Si and Ge.[9] However, the calculated ratio of phonon-assisted current to direct current was found to be 30 times smaller than the same ratio found from experiment.[4] An even greater discrepancy was observed when the magnitudes of the theoretical and experimental phonon-assisted tunneling currents were compared. The authors concluded that disagreement of the theory with experiment was not understood, although the effects of impurities within the narrow junction might be important.

In recent years, attention has been given to metal-semiconductor and metal-insulator-semiconductor tunnel junctions. The first report on InSb-oxide-metal junctions were made by Esaki[10] and Chang *et al.*[11] The latter authors have discussed the general character of the tunnel conductance at 4.2 °K for both n- and p-type InSb with carrier concentrations of 3×10^{18} and $10^{19}/cm^3$, respectively. A thin oxide layer was prepared on an etched crystal surface and the electrodes were either Sn or In. Structure was observed at 0.47 eV for the n-type semiconductor and it was assumed that this was due to tunneling to the L_1 conduction band, giving an energy difference between the minimum of this band and that at the zone center as $\Delta_{\Gamma\Lambda} = 0.75 \pm 0.5$ eV. A zero-bias minimum in conductance was observed for both n- and p-type InSb but no explanation was given.

An oscillatory tunnel conductance induced by LO phonons was reported by Katayama and Komatsubara[12] for n-type InSb junctions at 4.2 °K. Again the junction configuration was InSb-oxide metal but in this case the InSb carrier concentration was $2\times 10^{14}/cm^3$. Oscillations in the conductance had periodicity equal to 25 meV compared with the energy of the LO phonons, which is 24.4 meV.[13] A large conductance minimum was observed at +3 meV. The authors assumed that the conductance was a maximum for a reverse bias (metal negative) equal to $n\hbar\omega_{LO}$, with n integral, and these changes in the conductance were attributed to peaks in the InSb conduction-band density of states analogous to polaron-induced anomalies.

The observation by the present author of a very large number of phonon oscillations has stimulated a reinvestigation of the origin of these oscillations in both InSb-oxide-metal junctions and vacuum cleaved InSb-metal junctions. Approximately 30 oscillations of the conductance as a function of bias have been observed in both systems and interactions of the electrons with the TA and LA phonons have also been identified. The conductance of the samples has been studied as a function of both carrier concentration and temperature and a model for the junction is discussed. Some of these results on both types of junctions have been reported briefly.[14]

II. EXPERIMENTAL METHODS

The InSb single-crystal material was obtained from Cominco. The Hall-effect measurements[15] showed a carrier concentration of $6.8\times 10^{13}/cm^3$ and a resistivity of 0.68 Ω cm at 4.2 °K. Bars with cross sections 2×2 mm were cut with the [110] axis parallel to the long dimension and samples approximately 3 mm in length were cleaved from the bars.

A. Metal-Oxide-Semiconductor Junctions

The thermal oxidation of InSb has been studied in a series of papers by Rosenberg[16,17] and Rosenberg and Lavine.[18] At room temperature the rate of oxidation of the III-V compounds is small and for InSb in oxygen at a pressure of 400 μ the process saturates at approximately 2×10^{15} atoms of oxygen/cm^2. However, the total oxidation can be increased by up to 10^4 if the temperature of the crystal is raised to 500 °C. Rosenberg and Lavine[18] have also shown that, under the most favorable conditions, the oxide which forms on the surface is primarily In_2O_3 with the Sb forming a layer between the InSb and the oxide. Thus, approximately 2×10^{16} atoms of oxygen/cm^2 are required for an oxide 30 Å thick. In the present work, a sample was cleaved in air and placed on to an evaporating mask with 0.25-mm-diam holes. The front surface of the crystal was held off the mask by spacers and both the sample and the mask were heated to 300 °C in a vacuum of 10^{-8} Torr for approximately 5 h. Pure dry oxygen was admitted to a pressure of 750 μ and the sample was maintained at 300 °C for between 5 and 30 min. The chamber was again evacuated and, when the sample had cooled, the metal electrodes were evaporated on to the oxide. Finally, Ohmic electrodes of In:Ga (1:1) eutectic were painted on to a portion of the crystal from which the oxide had been removed either by polishing or cleaving. Contact to the injecting metal electrode was made by a gold ball pivoted on sapphire watch bearings and tensioned by a phosphor bronze spring.

B. Vacuum-Cleaved Junctions

An Ohmic contact of cerroseal alloy was first soldered to one end of a bar of InSb and a short copper lead was attached. The crystal was then placed into a cleaving apparatus which could be operated in a high vacuum of approximately 10^{-8} Torr. The electrode metal evaporation was started and the InSb was cleaved in the metal stream. The unwanted piece of crystal was removed by a spring and electrodes were deposited onto the cleaved surface through a mask with 0.25-mm-diam holes. Contact to the metal electrode was made with the gold ball, as mentioned above. By cleaving the crystals in this way, one could be sure that no oxide layer formed on the surface.

C. Capacitance Measurements

Space-charge capacitance measurements have been used by several authors to characterize Schottky barriers at metal-semiconductor interfaces. In particular, Goodman[19] and Goodman and Perkins[20] have formulated the theory for degenerate and nondegenerate semiconductors and

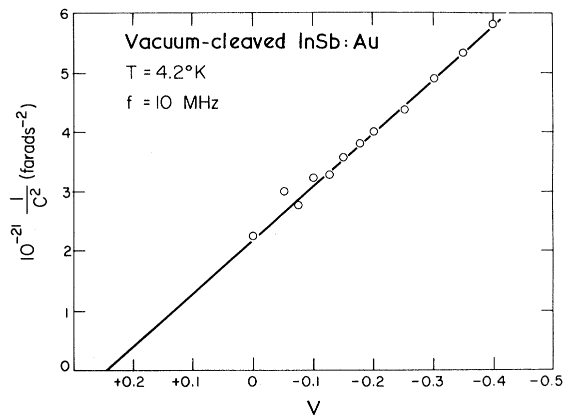

FIG. 1. Plot of C^{-2} vs bias voltage for a vacuum-cleaved InSb junction with a gold electrode. Measurement was made at a temperature of 4.2 °K and a frequency of 10 MHz.

have shown how the capacitance C can be used to measure the barrier height and the donor density by plotting C^{-2} vs V (the applied voltage). A series of such measurements has been carried out by Spitzer and Mead,[21,22] who have measured a barrier height of 0.17 ± 0.01 V for a gold contact on vacuum-cleaved InSb at 77 °K.

In the present work, the capacitance of several junctions was measured at 10 MHz on a rf impedance bridge with the sample at 4.2 °K. The stray capacitance of the bridge was reduced as much as possible but was still large and sometimes comparable with the value of capacitance being measured. No satisfactory measurements were possible on the oxide junction, but Fig. 1 shows the straight-line plot of C^{-2} vs V for a vacuum-cleaved sample with a gold electrode. The potential barrier height is given by the intercept with the voltage axis and is 0.24 ± 0.02 V.

This shows that the barrier height is approximately equal to the band gap of InSb, 0.24 eV at 4.2 °K, so that the metal Fermi level lies just within or at the edge of the valence band of the semiconductor. This is the complementary case to the InAs-metal system where the metal Fermi level lies in the conductance band of the p-type semiconductor.[23]

III. EXPERIMENTAL RESULTS

A. Oxide Junctions

The oxide junctions with gold contacts have a resistance at 4.2 °K of approximately 100 Ω. The I-V curves for these junctions show oscillations in the current which could easily be seen with an oscilloscope display when the bias was such that the metal electrode was negative (reverse bias). The differential conductance dI/dV of these samples shows very large oscillations as a function of bias voltage, as illustrated in Fig. 2 for a junction with 7×10^{13} carriers/cm^3 at 4.2 °K.

The curve is characterized by a sharp conductance minimum at zero bias, high forward-bias conductance, approximately constant conductance in reverse bias up to an energy of the order of the band gap, and then a steadily increasing conductance at higher reverse bias. If the positions of the *minima* are plotted as shown in Fig. 3, the slope of the curve gives a value of 26.3 ± 0.4 meV for the LO phonon energy and the intercept for zero phonons is 5 meV. Katayama and Komatsu-

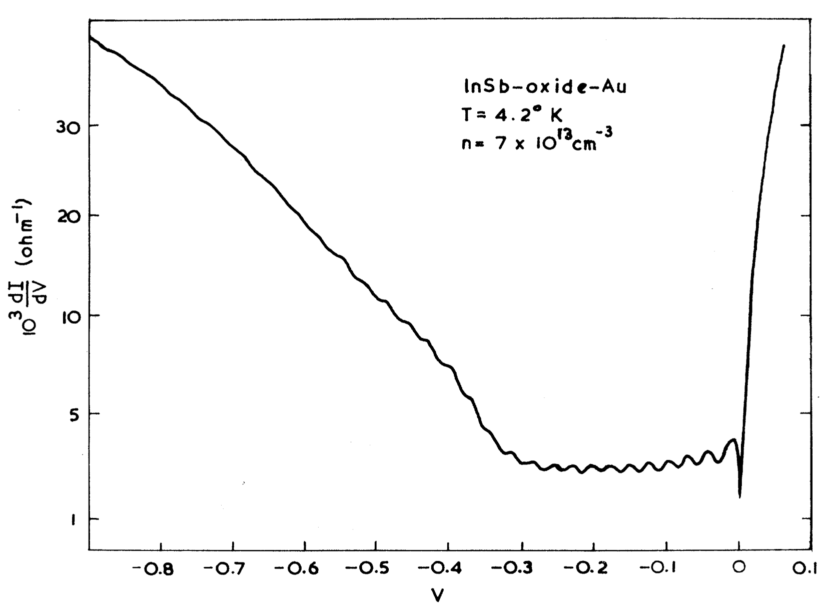

FIG. 2. Differential conductance of an oxide-coated InSb junction with a gold electrode. Approximately 30 LO phonon oscillations are observed.

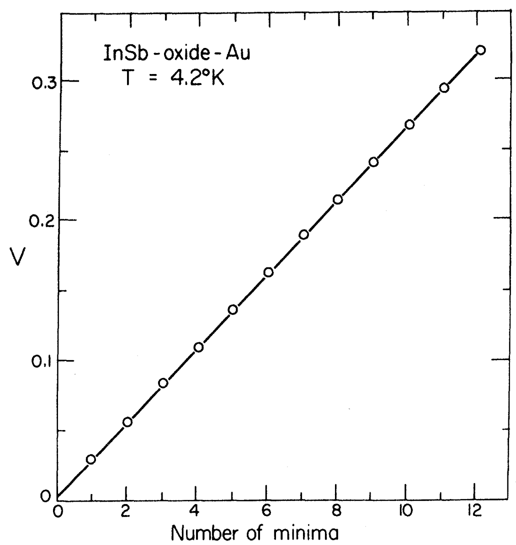

FIG. 3. Plot of the positions, in volts, of the oscillation minima vs the number of minima for an oxide-coated InSb junction at 4.2 °K. The slope gives an energy of 26.3 meV.

bara[12] have suggested that the conductance *maxima* occur when LO phonons are emitted but, if one considers the position of the first maximum at 15.1 meV, then it is clear that their interpretation is unsatisfactory. In fact, plotting the positions of the minima from their data gives a value of 26.8 meV, in agreement with the present measurements. Our choice of the minima to measure the phonon energy is supported in Sec. III B, where the results of the vacuum-cleaved samples are discussed.

Additional structure can be seen on the first few oscillations of the dI/dV curve and is more clearly observed in the second derivative spectrum, as shown in Fig. 4. The first submaximum is at 15 meV, close to the LA phonon energy of 14.6 meV, and repeats with LO phonon energy separation. The d^2I/dV^2 curve also allows an accurate measurement of the width of the zero-bias minimum; this is 10 ± 1 meV or twice the TA phonon energy, though the minimum is not symmetrical about $V=0$.

Junctions have also been prepared with Pb electrodes since the observation of the superconducting structure at zero bias confirms that the current is due to carriers tunneling from the superconductor. Very weak structure was observed superimposed on the zero-bias minimum. This minimum was broadened and displaced from $V=0$ though on application of a magnetic field the minimum moved back to $V=0$. However, no sharp structure, such as reported by McMillan and Rowell,[24] was observed, implying that the Pb electrode is not the injecting electrode.

The LO phonon structure in the differential conductance can be observed up to a temperature of 50 °K, but no zero-bias minimum is observed at this temperature. If the temperature is then lowered to 21 °K, the conductance minimum is observed at − 7.5 meV and, on further cooling, the minimum moves to $V=0$ at 4.2 °K. The temperature dependence of the magnitude of the zero-bias minimum is in qualitative agreement with the prediction of Bennett *et al.*[4] but it is not clear why the minimum shifts in energy as the temperature changes.

If the thickness of the oxide layer is increased, the junction conductance decreases and considerably more structure is observed. For instance, in Fig. 5 it is seen that a large positive zero-bias anomaly is superimposed on the conductance minimum. Such anomalies have been discussed in great detail by many authors[25,26] and experiments by

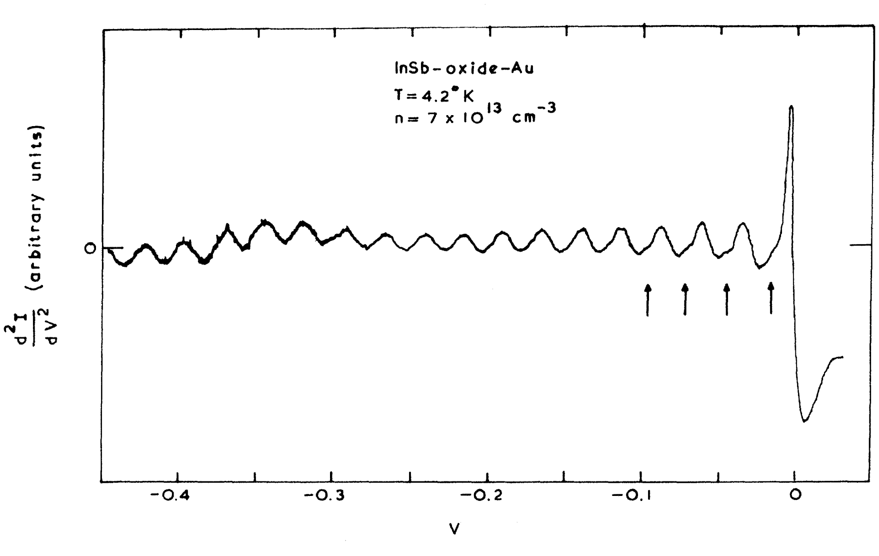

FIG. 4. Second-derivative conductance spectrum of an InSb-oxide-Au junction at 4.2 °K. A secondary oscillation series, marked by arrows, can be seen with the first structure occurring at the LA phonon energy.

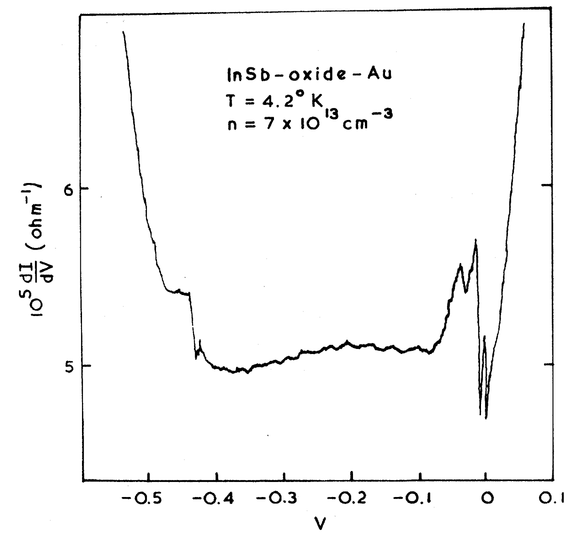

FIG. 5. Conductance spectrum of an InSb junction with a thick oxide film and a gold electrode. Phonon oscillations are weak and a zero-bias maximum is observed.

Tsui[27] have shown how interaction between the tunneling carriers and magnetic impurities in the barrier can produce a conductance maximum. The nature of the magnetic system formed during oxidation of the InSb has not been investigated. However, Fig. 5 is important since it shows how the phonon contribution to the conductance is substantially reduced when the junction resistance is high. For instance, the contribution in this case is 0.5% while for the thin oxide layers (Fig. 2) the contribution to the conductance is 20%. Thus the magnitude of the effect depends on the junction impedance which is consistent with the phonon interaction occurring in the semiconductor. This will be discussed in Sec. IV.

B. Vacuum-Cleaved Samples

The differential conductance of a sample with a gold electrode is shown in Fig. 6. The number of carriers in the sample was $7\times10^{13}/cm^3$ and the dI/dV measurement was made with the junction at 4.2 °K. The phonon structure and other features similar to the oxide-coated junctions can clearly be seen. For instance, a large conductance minimum is observed near zero bias and there is a sharp increase in the conductance at -0.24 V. The conductance in forward bias is high.

The first LO phonon minimum in reverse bias is at 26.5 meV and a plot of the positions of the first 10 minima is shown in Fig. 7. This gives an energy intercept of 2 meV and the spacing of the minima as 24.4 ± 0.2 meV, agreeing well with the same value of the LO phonon energy obtained from optical measurements. A small minimum is observed at 15 meV which corresponds to the LA phonon energy of 14.6 meV. Finally, a broad maximum which we associate with the InSb L_1 band has a threshold at -0.30 ± 0.01 V; it is observed in the oxide junctions (Fig. 2) as well, but not as clearly.

A study was made of the effect of changing the carrier concentration on the electron-phonon interaction, and the differential conductance of a sample with $6\times10^{14}/cm^3$ is shown in Fig. 8 for $T=4.2$ °K. Fewer oscillations are observed, there is a very

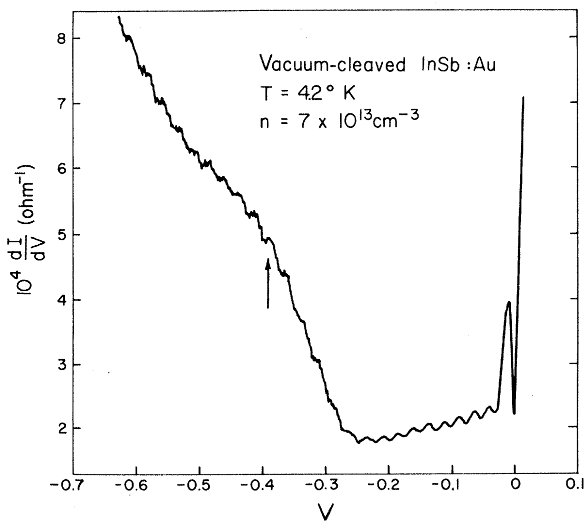

FIG. 6. Conductance of a vacuum-cleaved InSb junction with a gold electrode. Electron-hole pair formation is observed at $V=-0.24$ V and the arrow marks the conductance change due to carriers being excited to the L_1 band.

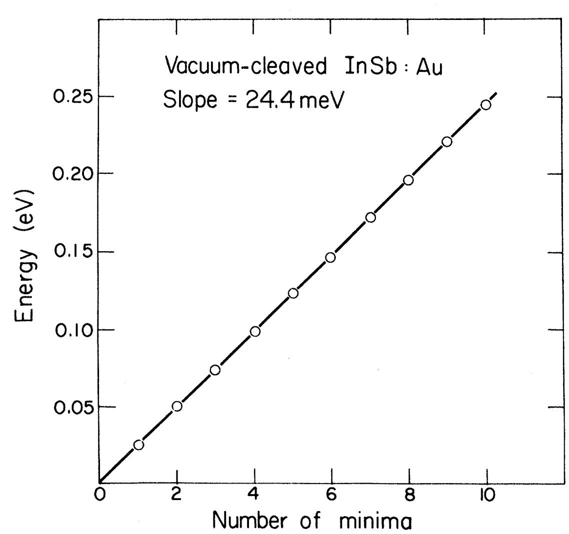

FIG. 7. Plot of the minima energies vs the number of minima for a vacuum-cleaved InSb junction with a gold electrode. The slope of the curve gives a value of 24.4 meV for the LO phonon energy.

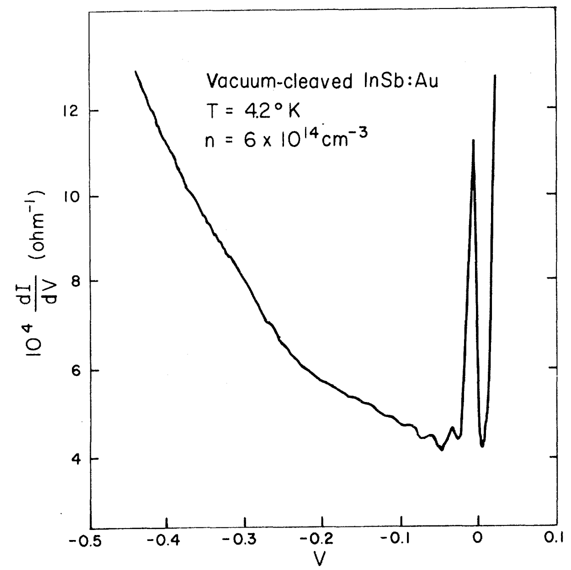

FIG. 8. Differential conductance of a vacuum-cleaved InSb junction with 6×10^{14} carriers/cm^3. Fewer phonon oscillations are observed.

large maximum in the conductance at -7 meV, and the minimum in the conductance is at $+5$ meV. The change in the conductance at -0.24 V is less pronounced. No phonon structure was observed in a junction prepared from InSb with 5×10^{15} carriers/cm^3, and so the effect diminishes with increasing carrier concentration.

The general shape of the differential conductance of a junction with a Pb electrode, as shown in Fig. 9, is similar to the junctions with gold electrodes. In addition, structure due to the superconducting properties of the Pb is observed at zero bias. Although the shape of the structure is correct, the magnitude is much smaller than one would expect if the total current flowed via the tunneling mechanism. For instance, Fig. 10 shows how the weak but sharp dip at zero bias is reduced in magnitude as the temperature is raised above the transition temperature of 7.2 °K. Above T_c there is no sign of the sharp dip with the phonon sidebands. A similar effect is observed when a magnetic field is applied. Figure 11 shows the zero-bias conductance for another sample with and without a magnetic field greater than the critical magnetic field. No superconducting structure is observed with the field on.

IV. DISCUSSION

A. Oscillatory Conductance

The differential conductance measurements of the InSb junctions show that at least 30 phonon oscillations can be observed; the change in conductance is as much as 20% of the mean conductance of the sample. Also, it is observed from a study of the vacuum-cleaved junctions that the oscillation minima occur when the injection energy equals multiples of the LO phonon energy, though the first minimum is always at an energy slightly greater

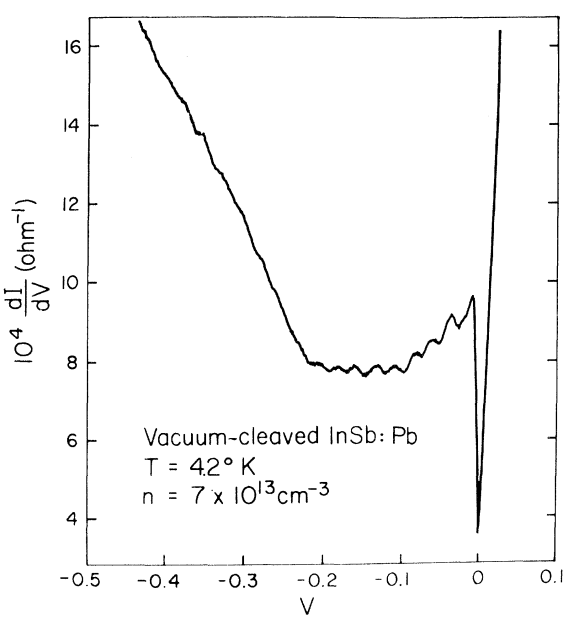

FIG. 9. Conductance of a vacuum-cleaved InSb junction with a Pb electrode.

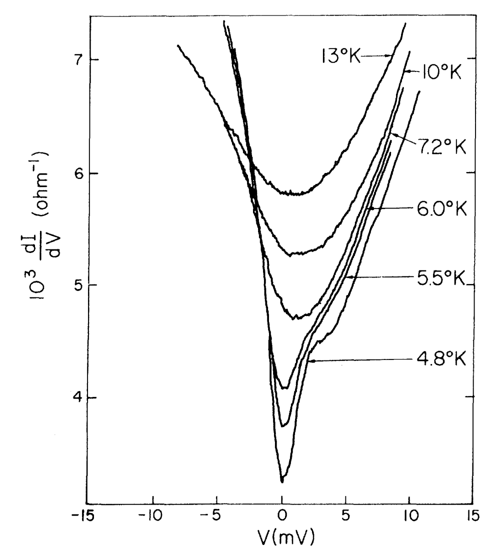

FIG. 10. Zero-bias structure due to the superconducting Pb electrode measured as a function of temperature. The junction is vacuum-cleaved InSb : Pb with 7×10^{13} carriers/cm^3 and the temperature is 4.2 °K.

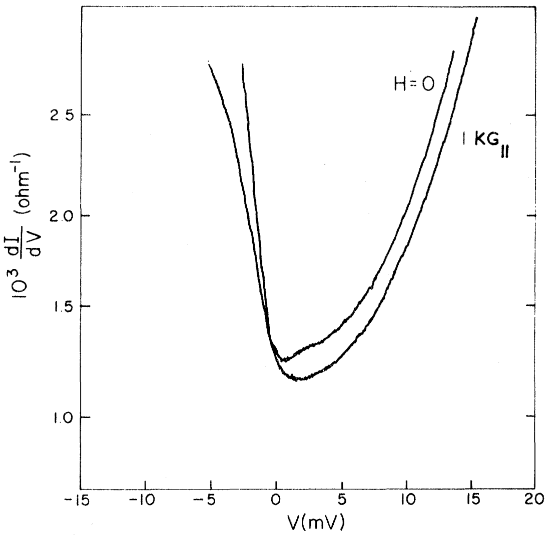

FIG. 11. Zero-bias structure due to the superconducting Pb electrode measured with and without a magnetic field greater than the critical field.

than the LO phonon energy. The perturbation interaction suggested by Katayama and Komatsubara[12] should predict peaks in the semiconductor conduction-band density of states at energies equal to multiples of the LO phonon energy, and so conductance maxima, not minima, should be observed. This effect should be vanishingly small at many phonon energies since the interaction is a phonon perturbation on the electron levels. Thus, the present observation of multiphonon emission suggests that the origin of the oscillations should be reconsidered.

A striking similarity exists between the conductance oscillations observed in the InSb junctions and the oscillatory photoconductivity reported for InSb single crystals by several authors.[28–32] In both experiments the oscillations are observed in approximately the same number and magnitude and the minimum photoconductance occurs at the LO phonon energies. Hence, we consider a model for the InSb junctions in which the electrons are injected into the bulk semiconductor, in analogy with the injection of carriers into the conduction band by light, as discussed by Stocker and Kaplan.[35] In both models the carriers lose energy by LO phonon emission until the energy of the electrons is between the semiconductor Fermi level and the energy of one optical phonon. Then, as the energy of the injected carriers changes, the conductance oscillates due to changes in the mobility with energy[33] or to changes in the electron energy distribution.[34–36] The uncertainty exists because no satisfactory explanation for the oscillatory photoconductivity has been agreed upon. (See Refs. 37 and 38.)

In the case of the InSb junctions, the injection model implies that the measured conductance is the sum of two components added in series. These are the junction conductance which occurs at the surface barrier and the oscillatory conductance which occurs in the bulk semiconductor. Since the bulk resistivity is very low (0.68 Ω cm at 4.2 °K), the oscillatory component can only be significant in the spreading resistance region of the bulk material, directly adjacent to the barrier region. In Table I the minimum resistance R and the peak-to-peak oscillatory component ΔR are compared for examples of three types of junctions. The value of R changes by 50 from the thin oxide junction to the thick oxide junction but the ΔR values are observed to be of the same order of magnitude, which is in agreement with the spreading resistance model since ΔR should be the same for all samples. The magnitude of the change in spreading resistance due to the electron-phonon interaction is not known, but in the oscillatory photoconductivity experiments, conductance changes of 30 to 100% are observed. A measurement of the InSb spreading resistances with two Ohmic contacts, one small and one large, showed that for a small contact of ~0.20-mm diameter the resistance was 145 Ω. This is the order of magnitude that one expects in the present case if ΔR is similar to that observed in the oscillatory photoconductivity experiments.

B. Inelastic Electron-Phonon Processes

The phonon emission processes are summarized in Fig. 12. For simplicity the oxide layer is not shown. In the barrier region inelastic tunneling takes place and the loss of TA phonons produces the zero-bias conductance minimum which has a measured half-width of $2\hbar\omega_{TA}$. The loss of TA phonons also shifts the first of the oscillatory conductance minima to a higher energy, equal to $\hbar\omega_{LO}+\hbar\omega_{TA}$. In the oxide junctions, a second oscillatory series is observed due to an inelastic process involving the LA phonons (see Fig. 4). The first minimum is at the LA phonon energy and subsequent minima are at $\hbar\omega_{LA}+n'\hbar\omega_{LO}$.

The impedance of the oxide junctions is always an order of magnitude less than that of the vacuum-cleaved junction. In fact, this low impedance and

TABLE I. Comparison of typical junction resistances R and amplitudes of the oscillatory components of the resistance, ΔR.

	R (Ω)	ΔR (Ω)	$\Delta R/R$ (%)
Oxide	360	80	20
Vac. cleaved	5000	250	5
Thick oxide	20 000	100	0.5

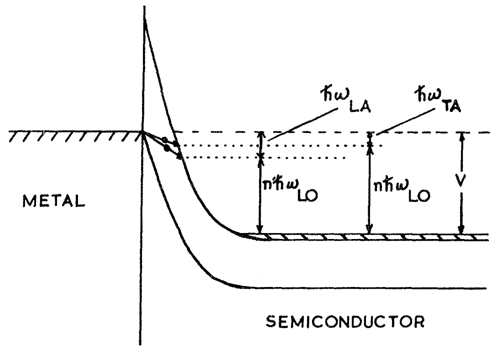

FIG. 12. Schematic model of InSb junction showing the observed inelastic scattering processes and the LO multiphonon emission. The applied voltage is denoted by V.

the absence of the expected superconducting structure with Pb contacts suggests that conduction through the oxide is via metallic pin-hole channels formed during the oxidation process. Metallic In and Sb can both be present in the oxide layer,[16] as the actual structure of the oxide layer depends very much on the preparation conditions. Evidence of pin-hole conduction giving rise to negative resistance in these junctions has been obtained by the author.[39] The presence of these conduction channels would account for the fact that the measured value of $\hbar\omega_{LO}$ for the oxide junction is 26.3 meV instead of 24.4 meV as measured with the vacuum-cleaved junctions; i.e., approximately 10% of the junction impedance is resistance of the filamentary conduction paths through the oxide layer.

In the vacuum-cleaved junctions, superconducting structure near zero bias is observed with the Pb electrodes, but it is small in magnitude, implying that the majority of the current carriers do not tunnel from the superconducting electrode. This is in agreement with the effects expected from the measured barrier height, which implies the presence of an inversion layer at the surface of the InSb so that the tunneling is from the valence band to the conduction band. The fact that weak superconducting structure is observed shows that the metal density of states is still important and so the inversion layer must be small. The zero-bias minimum is comparable in magnitude with that for the oxide junctions but the position of the minimum occurs in forward bias at a voltage equivalent to the Fermi energy for the n-type semiconductors; i.e., 1 meV for 7×10^{13} carriers/cm^3. It is not clear why the conductance minimum is unevenly spaced about zero bias. Finally, the LA phonon interaction is clearly observed in the vacuum-cleaved conductance spectra as a change in the slope of the conductance at 15 meV.

C. Excitation Processes in Bulk InSb

Electron-hole pair generation is observed in all junctions, occurring when the excitation energy reaches the band-gap energy of 0.24 eV at 4.2 °K. This is illustrated in Fig. 6 for the vacuum-cleaved junctions where a sharp increase in the conductance is observed when extra carriers are generated. For the oxide junctions, the energy of increase in conductance due to pair generation depends on the thickness of the oxide layer or filamentary conduction path (see Figs. 2 and 5). The conductance is further modified when the energy equals 0.39 ± 0.01 eV and for a vacuum-cleaved junction the position of the change of slope is marked in Fig. 6. This is interpreted as the result of carriers being excited from the Γ conduction band to the L_1 conduction band. Carriers which are excited to the upper L_1 conduction band will have a larger effective mass and hence the conductance increase is reduced, giving rise to the observed change in slope. Thus, the minimum of L_1 would be 0.63 ± 0.01 eV above the Γ maximum at the center of the zone. This value is considerably lower than the value of 0.75 calculated by Chang *et al.*[11] and slightly lower than the value of 0.69 eV predicted by Porowski *et al.*,[40] found from a study of the Gunn effect in InSb at 77 °K.

V. CONCLUSIONS

Theories of the oscillatory photoconductivity effect involving approximate or exact solutions of the Boltzmann equation have been proposed by several authors[34–36] and qualitative agreement with the experimental results has been achieved. However, quantitative agreement between the calculated and observed line shapes has not been found since the photoconductivity effect produces conductance changes which are oscillatory while the theories predict sharp conductance dips at the LO phonon energies. The conductance changes observed in the InSb junctions are undoubtedly oscillatory and so the same quantitative disagreement with the distribution function theory exists. Fan[37] and others[33,38] strongly support a theory involving a change of carrier mobility with energy, but so far no detailed theory exists and it is most likely that the oscillatory conductance is due to a combination of changes in both the electron distribution and the mobility. Unfortunately, the present experimental results do not clarify the interpretation since the constraints on the carriers which produce the oscillatory tunneling spectra are effectively the same as for the photoconductivity spectra, except for differences in recombination processes. However, it is clear that the electron tunneling technique can provide useful experimental details of electron distribution and band-structure effects in semiconductors.

In order to observe the oscillatory conductivity effect in other junctions, one must meet the criterion of low carrier concentration for a long electron mean free path and yet have a barrier with a resistance not very much greater than the series resistance. This may be achieved by constructing junctions with large contacts since the junction resistance is proportional to $1/r^2$, where r is the metal electrode radius, while the series resistance is approximately proportional to $1/r$, so that as r is made larger the series resistance becomes a larger proportion of the total junction resistance.

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