mostly of electrostatic origin, should scale like the inverse third power of the lattice constant a_0. This should yield a Raman frequency ν_0 proportional to $a_0^{-3/2}M^{-1/2}$ for the materials of the germanium family (M is the atomic mass). We have plotted in Fig. 2 the room-temperature values of ν_0 as a function of $a_0^{-3/2}M^{-1/2}$ for Si, Ge, and α-Sn[6]: The proportionality mentioned above is well satisfied. The Raman frequency of diamond[7] falls 10% below the line of Fig. 2. The simple-bond-charge model[8] predicts the following relationship between ν_0 and the bulk modulus B:

$$B = M(\pi\nu_0)^2/2a_0 \ . \qquad (1)$$

The value of B calculated with Fig. 1, $B_{\rm calc} = 5.4 \times 10^{11}$ dyn cm^{-2}, is in good agreement with that determined by Price and Rowe [$B_{\rm exp} = (5.3 \pm 1) \times 10^{11}$ dyn cm^{-2}] from the neutron-diffraction data for acoustical phonons.[4]

The Raman frequency of the single crystal at 273 °K [$\nu_0(273\,^\circ\text{K}) = (5.897 \pm 0.03) \times 10^{12}$ Hz] agrees well with that found for the polycrystalline sample at a slightly higher temperature [$\nu_0(297\,^\circ\text{K}) = (5.885 \pm 0.03) \times 10^{12}$ Hz]. The shift in ν_0 between 77 °K and room temperature is

$$\nu_0(77\,^\circ\text{K}) - \nu_0(297\,^\circ\text{K}) = (8.8 \pm 3) \times 10^{10} \text{ Hz} \ ,$$

comparable to that observed by Hart *et al.*[2] for Si in the same temperature range.

It is interesting to note that when hydrostatic pressure is applied to diamond,[9] Si,[10] or Ge,[11] ν_0 does not vary like a_0^{-2} but rather like a_0^{-3}. This stronger lattice-constant dependence is undoubtedly due to hard-core effects: The lattice becomes stiffer if one changes a_0 by compression than if one reduces a_0 by going from one material to another, thus reducing at the same time the atomic size. The observed temperature shift of ν_0, both for Si[2] and for α-Sn, is about four times larger than that naively predicted from the change of a_0 due to the thermal expansion.

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Electron Tunneling into $KTaO_3$ Schottky Barrier Junctions

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Electron tunneling techniques have been used to examine the characteristics of current (I) vs voltage (V) in degenerate n-type $KTaO_3$ Schottky barriers at 1 °K. The d^2V/dI^2-vs-V curve exhibits structure at each of the four LO modes in $KTaO_3$: 22.5, 34, 51.5, and 102.5 mV. Several two-phonon peaks were also seen and identified as 51.5 + 102.5 = 154-mV and 2 × 102.5 = 205-mV combinations. The almost antisymmetric nature of the phonon-induced structure about zero bias indicates that it is caused by the inelastic interaction of the tunneling electrons with phonons in the barrier. In addition, the maximum in the differential resistance dV/dI occurs at a bias equal to the Fermi level of the semiconductor, and an effective conduction-band mass $m^* = 0.5m_0$ of the free carriers has been determined.

I. INTRODUCTION

It is now well established that electron tunneling can be a primary mechanism for current transport in metal-semiconductor (MS) Schottky barriers.[1,2] In an n-type degenerate semiconductor, such as $KTaO_3$ used in this work, the barrier is characterized by a negative surface-charge density fol-

lowed by a positive uncompensated space-charge region whose width is inversely proportional to the square root of the carrier concentration.[3,4] Under the experimental conditions of high doping (10^{18} cm^{-3}) and low temperatures, where the barrier width is approximately 100 Å or less, it is now known that the numerical calculations of the coherent elastic conductances for Ge[5,6] and CdS[7] MS tunnel junctions are in accord with experimental values. In addition, contributions to the current arise via the interactions of the tunneling electrons with excitations such as phonons, plasmons, magnetic and nonmagnetic impurities, and self-energy effects in the semiconductor electrode.[1] In this paper the structure on the I-V, dV/dI, and d^2V/dI^2 curves at 1 °K, caused by the interaction of the tunneling electrons with the four LO phonons in $KTaO_3$, is presented. The three infrared-active LO modes are found to occur at 22.5, 51.5, and 102.5 mV, while the fourth "silent" mode (neither infrared- nor Raman-active) was at 34 mV. Two-phonon processes were also observed in which the tunneling electron presumably emits several LO phonons: These combinations were identified to be

$$\omega_{LO}^{(3)}+\omega_{LO}^{(4)} = 154 \text{ mV},$$

$$2\times\omega_{LO}^{(4)} = 205 \text{ mV}.$$

No evidence was found for two-phonon emission for any other combinations of LO modes or between LO and TO modes. The Fermi levels of the $KTaO_3$ crystals were experimentally determined by noting the (forward) bias at which the differential resistance dV/dI became a maximum.[4] Using a free-electron approximation, the effective mass in the conduction band was calculated to be $m^* = 0.5 m_0$. It should be noted that the above interpretation implicitly assumes that impurity-band tailing into the gap is negligible.

II. EXPERIMENTAL

Figure 1 shows a simplified energy-level diagram of a reverse-biased (metal electrode negative) MS contact at 0 °K. μ_M and μ_S are the Fermi degeneracies of the metal and semiconductor, V_B is the height of the Schottky barrier, d is the width of the depletion region, and E_G is the band gap. The arrows labeled a and b schematically show two possible tunneling channels for an electron at the Fermi level of the metal. a represents the usual elastic scattering through the potential barrier into empty states in the semiconductor. b is the inelastic channel associated with phonon emission; for LO phonons the b channel is open only for biases $|eV| \geq \hbar\omega_0$, where ω_0 is the phonon frequency. In the case of $KTaO_3$, inelastic electron scattering is found to be operative in all four LO modes and the threshold effects are readily observed.

$KTaO_3$ possesses a cubic perovskite structure with five atoms per unit cell, yielding fifteen degrees of freedom[8,9]; three of these are associated with the acoustic branches. Of the remaining twelve there are three (triply degenerate) silent modes, three LO modes, and three pairs of infrared-active TO modes. It is well known[8,10] that the frequency of the lowest TO mode decreases drastically as the temperature is lowered (the "soft mode"), and it accounts for the large temperature dependence of the static dielectric constant.[11,12]

Previous studies of Schottky barriers on $KTaO_3$ have been made by Wemple and co-workers. These include transport properties,[11] nonlinear polarization studies,[12] optical measurements,[13] room-temperature capacitance I-V, and photoresponse data.[14] The $KTaO_3$ crystals used were extrinsic n type (presumably due to oxygen deficiencies) with a room-temperature optical band gap of 3.5 eV.[11] The sample surfaces were prepared by two different methods: (a) chemical etch and (b) cleavage in air. Both methods produced identical results in the dV/dI and d^2V/dI^2 curves concerning the qualitative features and positions of the phonon structure. However, the chemically prepared units always displayed larger resistances. The crystals were etched by placing them in a molten solution of KOH for approximately 5 min and subsequent multiple rinses in boiling distilled water using an ultrasonic cleaner. The Schottky or "blocking" contacts were formed on one surface of the crystal by vacuum deposition of 2×10^{-3}-cm^2 In dots. In was chosen because tunneling can be confirmed, at least for small biases, by the observation of the In superconducting

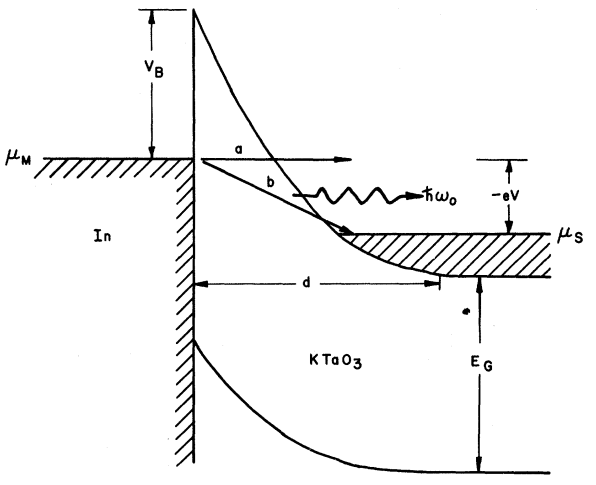

FIG. 1. Reverse-biased metal-semiconductor junction. Process a represents elastic tunneling of an electron near the Fermi surface of the metal electrode, while b shows an inelastic process via phonon emission. Other symbols are explained in the text.

energy gap below $T_c = 3.4\,^{\circ}\mathrm{K}$. The Ohmic contacts were formed by rubbing an In-Ga amalgam on the reverse side of the crystal with the aid of an ultrasonic soldering iron. The crystal was then connected to a derivative circuit using the standard four-terminal technique, immersed in liquid helium, and cooled to a temperature of $1\,^{\circ}\mathrm{K}$. The first and second derivatives, dV/dI and d^2V/dI^2, were obtained by well-known methods[15,16] and the constant current modulation was such that the voltage modulation across the Schottky barrier never exceeded 200 μV rms. Three crystals with carrier concentrations of 3.2, 6.3, and 8×10^{18} cm^{-3} were examined and all gave the same qualitative results.

Figure 2 shows the I-V and dV/dI curves for the 8×10^{18}-cm^{-3} sample. A small portion of the I-V curve in reverse bias (metal electrode negative) is shown to indicate the strong rectification: Similar rectification has also been observed in degenerate n-type $SrTiO_3$.[17,18] The large peak in the dV/dI curve that occurs near zero bias is due to the In superconducting energy gap. Figure 3 shows the second derivative d^2V/dI^2 for forward bias.

The positions of the four LO modes are clearly indicated and the values of the three IR-active modes 22.5, 51.5, and 102.5 mV are comparable with those estimated by infrared measurements of 23.4, 52.5, and 103.5 mV.[9,19] It should be mentioned that electron tunneling is the only technique that has directly measured all four LO modes, which includes the silent mode at 34 mV. Inelastic neutron scattering could also yield this information although the only data that exist are on the temperature dependence of the soft mode.[10] Two-phonon processes corresponding to $\omega_{LO}^{(3)}+\omega_{LO}^{(4)}$ and $2\times\omega_{LO}^{(4)}$ can also be seen (we are using the notation of Ref. 8). The $2\times\omega_{LO}^{(3)}$ probably also occurs, but its position lies at 103 mV and is masked by the position of the $\omega_{LO}^{(4)}$ mode. The two lowest-frequency LO modes $\omega_{LO}^{(1)}$ and $\omega_{LO}^{(2)}$ exhibit the weakest structure on the curves and no two-phonon peaks were observed for these, although $2\times\omega_{LO}^{(2)}$ has been seen in the second-order Raman spectra.[20] The position of the lowest-frequency ("soft") mode $\omega_{TO}^{(1)}$ is made uncertain because of the strong variable electric fields present in the Schottky region. This point will be elaborated further on in this section.

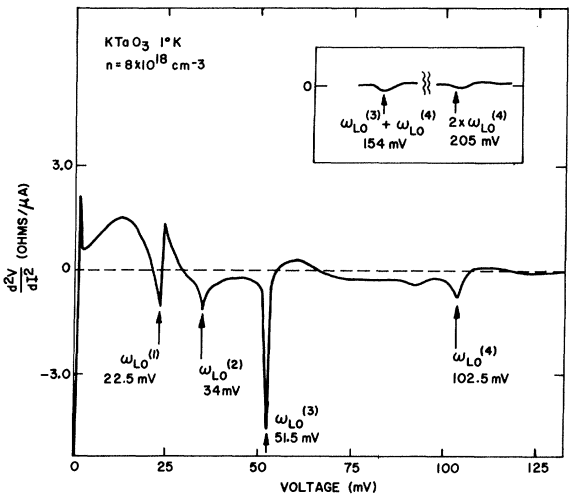

FIG. 3. d^2V/dI^2-vs-V curve for forward bias.

The phonon structure on the d^2V/dI^2 curves of Figs. 3 and 4 is approximately antisymmetric about zero bias which indicates that the structure is possibly caused by inelastic phonon emission in the barrier region, although self-energy effects in the $KTaO_3$ electrode cannot be entirely ruled out because of changes in screening in the space-charge region.[21] Also, we have seen no evidence for the interaction of tunneling electrons with any of the four TO modes. Infrared and Raman measurements place $\omega_{TO}^{(2)}$ and $\omega_{TO}^{(4)}$ at 24.7 and 68.2 mV, respectively.[8,9,10] $\omega_{TO}^{(3)}$, being neither Raman- nor IR-active, is thought to occur at 34 mV and is degenerate with $\omega_{LO}^{(2)}$. An examination of Fig. 2 shows that the phonon structure is displayed as a dip in the differential resistance rather than the usual step that has been observed for inelastic processes

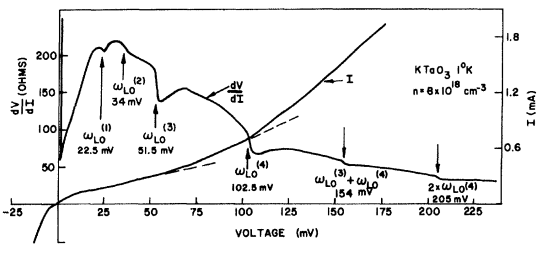

FIG. 2. I and dV/dI vs V for n-$KTaO_3$ showing the positions of the four LO phonons as well as several two-phonon processes.

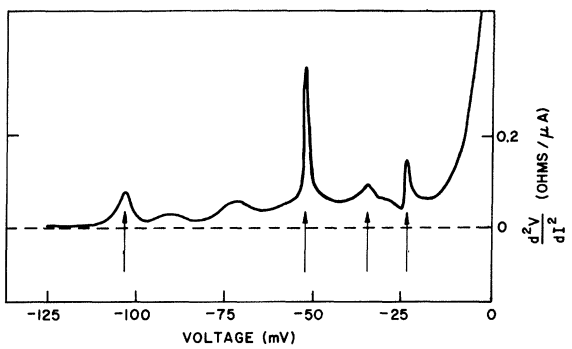

FIG. 4. d^2V/dI^2 vs V for reverse bias.

in metal-insulator-metal junctions. The dip is possibly caused by the relatively narrow Fermi level in the semiconductor. At $eV = \hbar\omega_0$, the inelastic process occurs and the differential resistance drops. For $\hbar\omega_0 < eV < \hbar\omega_0 + \mu_s$, the number of current-carrying states increases in the $KTaO_3$ and the resistance remains smaller than when $V < \hbar\omega_0$. However, for $V > \hbar\omega_0 + \mu_s$, there are no new current states available in the semiconductor and the differential resistance returns approximately to its value when $V < \hbar\omega_0$. In addition to the phonon structure there is an additional dip occurring at approximately 90 mV in the d^2V/dI^2 curve (Fig. 3). This dip was present in all three samples and remains unexplained.

Conley *et al.*[4] have pointed out that, under certain conditions, the maximum in the dV/dI curve occurring in forward bias corresponds to the Fermi level of the n-type semiconductor. Conley and Mahan[22] have shown that this is true when (i) $V_B/E_G < 0.5$, where V_B is the height of the Schottky barrier and E_G is the band gap (see Fig. 1), and (ii) when $\mu_s/E_0 \leq 1$, where μ_s is the Fermi degeneracy of the semiconductor and $E_0 = e\hbar(\pi N/m^*\epsilon)^{1/2}$ (cgs units). N is the carrier concentration, m^* is the effective mass, and ϵ is the static dielectric constant in the barrier region. Condition (i) implies that a one-band model of the semiconductor, such as that used by Conley *et al.*,[4] is adequate for describing the electronic dispersion in the Schottky region. The second condition ensures that electrons at the bottom of the conduction band can tunnel almost as easily as those at the Fermi level, which produces a maximum in the dV/dI curve at a bias equal to the Fermi degeneracy. Capacitance measurements have yielded a value of $V_B \sim 1.4$ V and $E_G = 3.5$ V, so that condition (i) is satisfied. However, the presence of the "soft" mode causes an extremely large dielectric constant at 4.2 °K ($\epsilon \approx 4430$ in the absence of external fields) and it would appear that condition (ii) is violated because $E_0 \sim 1\,\text{mV} \ll \mu_s$. There is experimental evidence that the value of ϵ in the Schottky region must be greatly reduced from the bulk paraelectric value of 4430. First, the thickness d of the barrier (see Fig. 1) is proportional to $\sqrt{\epsilon}$. Such large values of ϵ would yield thicknesses of several thousand angstroms and no tunneling would be observed. Second, the condition that $E_0 \ll \mu_s$ implies that the maximum in dV/dI would shift to significantly smaller values of the bias.[22] This is not the case in $KTaO_3$ because the maximum (see Fig. 2) occurs at 28 ± 4 mV ($N = 8\times10^{18}$ cm^{-3}) which equals the calculated free-electron value if one uses a value of $\sim 0.5m_0$ for the effective mass. It is reasonable to assume that ϵ must be drastically reduced by the strong electric fields present in the barrier region.[8,12] Electric-field-induced Raman studies[8,23] on both $KTaO_3$ and $SrTiO_3$ have shown that the field-dependent "soft" mode causes ϵ to decrease rapidly with increasing electric field strengths. In the Schottky barrier, the electric field strength is strongest at the metal-semiconductor surface and decreases rapidly with increasing distance into the barrier. Therefore, the field-dependent dielectric constant is also a function of position in the depletion region, and a unique value of ϵ cannot be assigned to the junction. However, it is possible to calculate an "effective" dielectric constant ϵ_{eff} for the depletion region by noting that, for large forward biases, the current in an MS junction should follow the exponential form $I \sim e^{V/E_0}$, where V is the applied voltage.[22] For our junctions the above relation is obeyed for $V > 300$ mV and can be fit using a value of $E_0 = 35$ mV. Therefore, the effective dielectric constant is

$$\epsilon_{eff} = \pi e^2\hbar^2 N/m^* E_0^2 \approx 5$$

for $N = 8\times10^{18}$ cm^{-3} and $m^* = 0.5m_0$. This number cannot be taken too seriously and represents only a lower limit. First, the above equation was derived on the basis that ϵ was constant throughout the barrier, and this assumption is not true here. Second, at high field strengths ϵ saturates at some limiting value which is probably higher than $\epsilon = 5$ which represents the electronic contribution to the index of refraction in the bulk material. However, the above does suggest that the strong fields in the region ($\sim 10^6$ V/cm at the metal-semiconductor surface) produce an effective dielectric constant which is considerably less than the field-free value at 4 °K.

The measurement of the Fermi level for the three different carrier concentrations used yielded an average density-of-states mass of $m^* = 0.5 \pm 0.07$. The error in determining m^* arises principally from the uncertainty in determining the peak of the differential resistance. Since the Fermi level E_F is given by

$$E_F = (\hbar^2/2m^*)(3\pi^2 N)^{2/3},$$

then $\delta m^* = m^*(\delta E_F/E_F) = 0.07$. It is difficult to compare this number with existing theoretical data because no band-structure calculations are available, although the measured value of m^* is in accord with other experimental values. A value of $m^* = (0.8 \pm 0.28)m_0$ has been calculated by measuring the room-temperature Seebeck coefficient.[11] Cyclotron-resonance measurements[24] at 1.4 °K have yielded an anisotropic effective mass with a mean value of $0.5m_0$ which agrees with the tunneling results. The effective "bare" band mass (not the polaron mass) has been found from Faraday rotation measurements to be $m^* = 0.42m_0$.[25] The polaron mass is expected to be approximately 30%

larger than the band mass which would yield a value of $m^* \approx 0.55m_0$. Magnetoresistive measurements[26] can then give the longitudinal m_l and transverse m_t effective masses in $KTaO_3$. Using $K = m_l/m_t = 4.4$, $m^* = 0.5$, and a three-spheroid model, one obtains $m_l = 0.67m_0$ and $m_t = 0.15m_0$.

III. CONCLUSION

In summary, the interaction of tunneling electrons with the four LO modes has been observed for the first time in n-type degenerate $KTaO_3$ at 1 °K. For three of the modes $\omega_{LO}^{(1)}$, $\omega_{LO}^{(3)}$, and $\omega_{LO}^{(4)}$ the interaction is via polar coupling since these modes are IR active. The mode $\omega_{LO}^{(2)}$ at 34 mV is neither IR nor Raman active and the interaction is due to the deformation potential. Several two-phonon peaks were also observed and corresponded to $\omega_{LO}^{(3)} + \omega_{LO}^{(4)}$ and $2\times\omega_{LO}^{(4)}$. The presence of the field- and temperature-dependent "soft" mode causes the dielectric constant in the Schottky region to vary substantially with distance because of the strong electric field. By observing the dependence of the current on the applied voltage it was possible to deduce an "effective" dielectric constant $\epsilon_{eff} \approx 5$ which is sharply reduced from the field-free paraelectric value of $\epsilon = 4430$ at 4 °K. Finally, the Fermi levels were determined for three different values of the carrier concentration by measuring the (forward) bias where the differential resistance was a maximum. Under the assumption of negligible band tailing, an effective density-of-states mass of $m^* \approx 0.5m_0$ was calculated.

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