part, CBHA, and $P_m = 0$ when $c = 0.93$ [Figs. 3(a) and 3(b)]. Our model (Fig. 2) is not compatible with monolayer smectics exhibiting the reentrant nematic phase.

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Observation of Electronic Band-Structure Effects on Impact Ionization by Temperature Tuning

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Impact ionization in semiconductors is shown to be strongly affected by temperature-tuning the band structure. In ⟨100⟩ GaAs between 25 and 150°C the hole ionization rate β is greater than the electron rate α, whereas above this temperature α becomes greater than β. This effect is attributed to the sudden lowering of the electron threshold ionization energy close to 200°C and is shown to be evidence for the existence of the pseudogap between the Γ_6-X_6 and Γ_7-X_7 conduction bands.

We demonstrate for the first time that the relative magnitudes of impact-ionization rates for electrons and holes in semiconductors can be reversed by temperature tuning. In ⟨100⟩ GaAs at room temperature, the ionization rate for holes, β, is greater than that for electrons, α, whereas at 200°C and above the opposite occurs. The main features of this effect may be explained in terms of a simple model based on the band structure, which predicts an abrupt change in the electron threshold ionization energy near 200°C. These results shed new light on the relationship of impact ionization to electronic band structure, and at the same time provide a new method of probing high-energy-band regions not previously explored. In particular, we present the first experimental evidence for the existence of the theoretically predicted pseudogap in ⟨100⟩ GaAs between the Γ_6-X_6 and Γ_7-X_7 conduction bands.

Measurements were made in the field region of GaAs p-n homojunctions grown by liquid-phase epitaxy on ⟨100⟩ Sn-doped GaAs substrates. These samples were one-sided, abrupt junctions with n-side and p-side dopings of $n \approx 2.6\times10^{16}$ cm^{-3} and $p \approx 2\times10^{18}$ cm^{-3}, respectively, and had a maximum electric field at breakdown of $E_m \approx 5\times10^5$ V cm^{-1}. Avalanche multiplication was measured by optically exciting free carriers and monitoring the photocurrent as a function of reverse bias voltage for several ambient temperatures, with the diodes mounted on a heater in a dry nitrogen atmosphere. The samples were processed photolithographically into the configuration illustrated in the inset of Fig. 1 so that low-intensity ($\approx 10^{-5}$

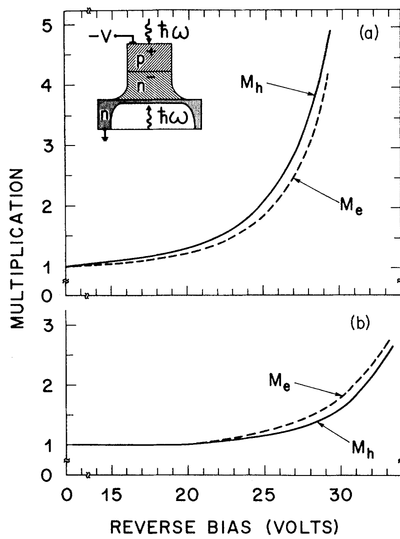

FIG. 1. Experimental multiplication data for avalanche gain initiated by holes (M_h) and electrons (M_e) in a typical ⟨100⟩ GaAs diode at (a) 25°C and (b) 200°C. Within the experimental error of a few percent, these curves were reproduced for optical injection at several points on the diode. The inset shows a schematic diagram of the experimental configuration.

W) 6328-Å laser radiation could be coupled into either the p-side or the n-side layers within a few microns of the junction. This arrangement allows the direct determination of the electron-initiated (M_e) and the hole-initiated (M_h) multiplications, which were deduced by taking the ratio of the multiplied photocurrent to the linearly extrapolated low-field photocurrent.[1-3]

Figure 1 shows the multiplication data versus reverse bias at 25 and 200°C for a typical diode. The data at 25°C show clearly that $M_h > M_e$ over the entire voltage range. In the best diode, at 25°C, gains as high as $M_h = 50$ and $M_e = 40$ were observed, well before the onset of microplasma breakdown. At 200°C the multiplication behavior is reversed, with $M_e > M_h$. Note the shift to higher voltage of the multiplication data with temperature, which is consistent with the well-known behavior of the avalanche breakdown voltage. This is the first time that the relative magnitudes of the multiplications initiated by electrons and holes have been shown to be reversible by temperature tuning.

The variation of M_h and M_e over the range from 25 to 250°C, at a fixed field of $E_m = 4.3 \times 10^5$ V cm^{-1}, is presented in Fig. 2(a) in the form $\ln(M_h/M_e)$ versus temperature for two different diodes. Up to 150°C this quantity remains relatively constant, whereas above this temperature a change

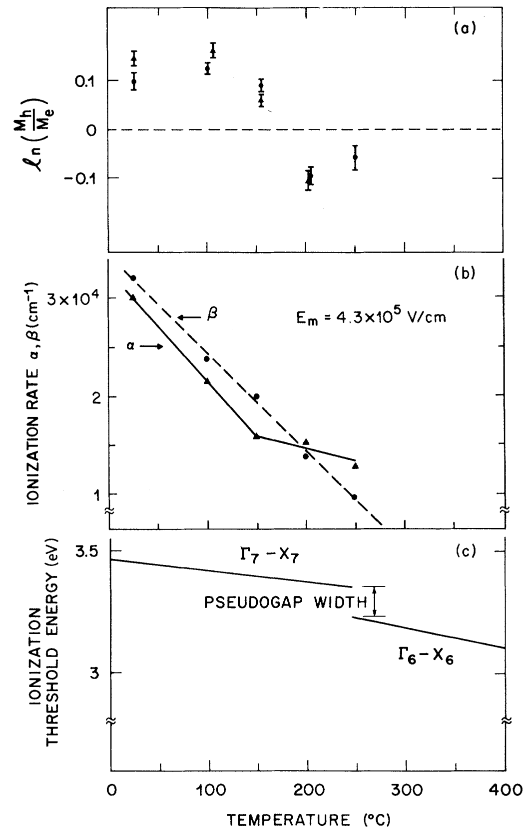

FIG. 2. (a) $\ln(M_h/M_e)$ vs temperature for two different diodes at a fixed maximum junction field $E_m = 4.3 \times 10^5$ V cm^{-1}. (b) Impact ionization rates α and β vs temperature, at the same field as in (a), for one of the diodes. The lines are drawn only to connect the data points. Similar results were observed in two other diodes. (c) Electron threshold ionization energy, measured with respect to the top of the valence band, vs temperature, calculated from the band structure of ⟨100⟩ GaAs.

in sign occurs. The significance of $\ln(M_h/M_e)$ is that it represents the excess of the number of secondary pairs created by a hole [$N_h(W)$] with respect to the number created by an electron [$N_e(W)$] while crossing the entire depletion region width W. This can be seen from the relationship[4]

$$\ln\frac{M_h(W)}{M_e(W)} = \int_0^W [\beta(z) - \alpha(z)]\,dz = N_h(W) - N_e(W), \qquad (1)$$

where the ionization rates $\alpha(z)$ and $\beta(z)$ are the numbers of secondary pairs created per unit path length by an electron and a hole, respectively. Thus the data of Fig. 2(a) suggest that α and β themselves undergo a change in behavior in the vicinity of 200°C.

These ionization rates, as functions of the max-

imum junction field E_m, can be directly obtained from M_h and M_e using[2,4]

$$\alpha(E_m)=\beta(E_m)+\frac{d}{dW}\left[\ln\left(\frac{M_e}{M_h}\right)\right] \quad (2)$$

and

$$\beta(E_m)=\frac{1}{M_e}\frac{d}{dW}[\ln M_h]. \quad (3)$$

Figure 2(b) shows α and β, determined in this way, as functions of temperature for one of the diodes at $E_m = 4.3\times10^5$ V cm^{-1}. Over the entire range β decreases smoothly with temperature. In contrast, α exhibits a change in behavior above 150°C. These effects are observed over the entire field range investigated, from 4×10^5 to 5×10^5 V cm^{-1}, with the change in α being somewhat more pronounced at the lower fields. Although the general decrease of both α and β with temperature is expected because of increased phonon scattering, it is clear from Fig. 2(b) that the electron ionization rate has a more complicated dependence, presumably due to some additional process.

Previous work has suggested that the ionization rates are critically related to the electronic band structure through the magnitude and position of the threshold ionization energies for electrons and holes.[2,5-7] To interpret our results, we have therefore calculated the temperature dependence of the threshold ionization energies using the most recently available band structure,[8] and the method of Anderson and Crowell.[5] The effect of temperature was introduced in a simple way. For each temperature the entire conduction-band structure was rigidly adjusted relative to the valence bands so that the direct band gap agreed with experiment.[9] This simple approximation, made because the detailed temperature variation of the entire energy-band structure is not known, is nevertheless reasonable since the band-gap shift is small (< 0.1 eV) compared with either the band-gap energy (≈ 1.4 eV) or the width of the conduction band (≈ 1 eV).

The results of the calculation for electrons are given in Fig. 2(c), which shows the threshold ionization energy as a function of temperature. Note the step in energy, which is related to the existence of the pseudogap between the Γ_6-X_6 and Γ Γ_7-X_7 conduction bands (near $k/k_{max} = 0.3$), as seen in Fig. 3, the electronic band structure for ⟨100⟩ GaAs.[8] For temperatures below ≈ 240°C, an electron can achieve the conditions for impact ionization only in the upper Γ_7-X_7 band, which

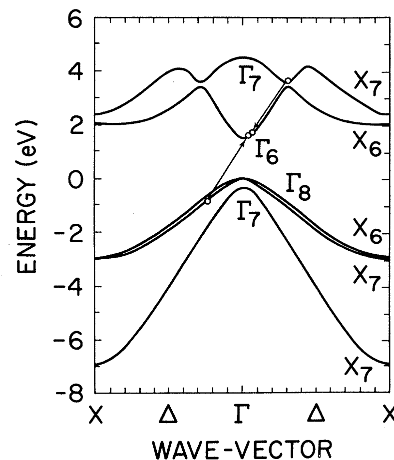

FIG. 3. GaAs electronic band structure in the ⟨100⟩ direction as obtained from nonlocal pseudopotential calculations (Ref. 8). The arrows and dots indicate the impact-ionization process at room temperature initiated by an electron which has tunneled through the pseudogap to threshold in the Γ_7-X_7 band.

would require the electron to tunnel across the pseudogap. At 240°C or higher, however, the gap between the valence band Γ_8 and the first conduction band Γ_6 has shrunk enough, because of the temperature rise, to allow an electron to initiate impact ionization in the lower band Γ_6-X_6 very near the pseudogap, so that no tunneling process is necessary. The step in the electron threshold energy seen in Fig. 2(c) is thus just the width of the pseudogap, ≈ 0.12 eV. In contrast, the threshold ionization energy of the holes varies smoothly with temperature, consistent with the smooth variation of β in Fig. 2(b). We therefore attribute the change in the relative magnitudes of the observed ionization rates to the change in the *electron* threshold ionization energy.

The simple model introduced here provides an explanation for the essential feature of the experiment, the reversal of the ionization rates near 200°C. The scattering mechanisms (phonons, etc.) which give rise to the general decrease of α and β with temperature are not expected to have a significant effect on the observed reversal. Further, the strong electric fields (> 10^5 V cm^{-1}) of the experiment, which might create band tails in the band gap[10] (like the ones responsible for the Franz-Keldysh shift of the absorption edge) and modify the effective ionization energy, would only be expected to make the step with temperature more gradual. Finally, the pseudopotential calculations predict only an approximate band structure in the pseudogap region. Nevertheless, the

present experiment shows that the predicted width of the pseudogap, 0.12 eV, is quite reasonable. In fact, the connection between impact ionization and the electronic band structure suggests the further use of impact-ionization experiments as a means of probing high-energy-band regions

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Observation of a Magnetic Modulation of the Lattice Electric-Field Gradient of Fe^{2+} Substituted in $1T$-TaS_2

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An unusual temperature dependence of the quadrupole splitting of Fe^{2+} in $1T$-$Fe_{0.1}Ta_{0.9}S_2$ can be understood in terms of a magnetic modulation of the *lattice* electric-field gradient. This modulation is produced by a strictive interaction between the local lattice environment and the continuous low-spin–high-spin transition of Fe^{2+}. The onset of the charge-density-wave instability can also be observed.

There has recently been an active interest in the literature both in the origin of the temperature dependence of the electric-field gradient (EFG) in noncubic metals[1-3] and in the existence of charge-density-wave (CDW) instabilities[4,5] in the d^1 layer transition-metal dichalcogenides like $1T$-TaS_2. The former concerns the screening role played by itinerant electrons while the latter involves electronically driven lattice instabilities. These interests, and also those concerning low-spin (LS)–high-spin (HS) transitions in $3d$ transition-metal ions, can all be combined in a study of the Mössbauer quadrupole splitting (QS) in iron-doped $1T$-TaS_2. Here we report the temperature dependence of QS for $1T$-$Fe_{0.4}Ta_{0.9}S_2$ which shows unusual behavior completely unlike any metallic or insulator compound yet studied. We show that the anomalous character is produced by a temperature modulation of the EFG caused by a perturbation of the local Fe^{2+} environment by the continuous LS-HS transition of Fe^{2+} with increasing temperature T.

The magnetic susceptibility and Mössbauer isomer shift[6] in $1T$-$Fe_xTa_{1-x}S_2$ ($x \leq \frac{1}{3}$) demonstrated the presence of a dynamic LS-HS transition of Fe^{2+} with increasing T. It was established that the iron was present solely as Fe^{2+}, that its magnetic electrons were localized, and that the LS-HS energy gap was significantly modulated as a function of T by a strictive interaction with the local lattice environment. As a result of this interaction, the mean displacement coordinate of local ion motion is modulated in a distinctive manner as a thermal population of HS levels takes place.

Mössbauer absorption spectra were taken in transmission geometry using the conventional technique.[7] Each spectrum shows two resonance