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correlations of electrons are present (e.g., 4 or 6) these will give rise to subharmonic or lower order

harmonic steps and not affect the voltage at which the steps appear.

REFLECTANCE MODULATION BY THE SURFACE FIELD IN GaAs

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By studying reflectance spectra in GaAs modulated by a second, intense light beam, we have observed oscillatory structures in the spectra near the energy gap as well as near 3 eV. We conclude that these structures result from a neutralization of the builtin surface field by free carriers created by the intense light beam. The experimental line shape near the band gap is qualitatively very similar to the theoretical prediction for the Franz-Keldysh effect but is shifted to lower energies presumably due to exciton effects.

We report photoreflectance (PR) experiments at 77° and 294°K in GaAs in which the reflectivity is modulated by a second, intense light beam. PR experiments were first reported by Wang, Albers, and Bleil¹ for several materials at room temperature. These authors suggested that the reflectance is modulated by the built-in surface field which is periodically neutralized by the free carriers created by the intense light beam. Gay and Klauder² have recently proposed that the PR effect observed by Wang, Albers, and Bleil¹ is due to a change in the effective density of states produced by the photoexcited carriers via the Pauli principle, i.e., band filling. On the other hand, if the modulation is in fact produced by an electric field, its origin may be either the Dember field which arises from the difference in mobility of the photoexcited electrons and holes or the neutralization of the surface field. The results reported here allow us to identify the mechanism responsible for photoreflectance in GaAs.

As the source of the modulating light we have used a He-Ne laser at 6328 Å to facilitate studies of the dependence of the PR line shape upon the intensity of the modulating beam. The various mechanisms proposed to explain the PR effect differ in the predicted dependence of the line shape upon the intensity of the modulating beam. Both light beams were near normal incidence on the samples and the laser was chopped at 510 Hz. Our experiments were performed on as-grown surfaces of high-purity epitaxial layers grown by K. L. Lawley at Bell Telephone Laboratories. Both *n*-type and *p*-type samples with impurity concentrations in the range 10^{15} to 10^{16} cm⁻³ were used. For the experiments at 77°K the sample was immersed in liquid nitrogen. Assuming nucleate boiling of the liquid nitrogen³ the average laser power of 0.150 W/cm^2 raised the temperature of the sample at most ~2°K above the temperature of the bath. The periodic temperature variation at 510 Hz was, of course, much smaller. From the known thermal diffusivity⁴ of GaAs we estimate⁵ that the peakto-peak temperature swing at 510 Hz was ~0.015°K.

In Fig. 1 we present the PR spectrum for photon energies near the band gap in GaAs for both 77 and 294°K. At both temperatures, six peaks are resolved with the spacing of the peaks being somewhat smaller at 77°K than at 294°K. In addition, a very sharp spike labeled *B* in Fig. 1 appears at 77°K. Apart from this spike, which will be discussed in a later section, the PR line shape is qualitatively very similar to the theoret-



FIG. 1. Photoreflectance spectrum for photon energies near the band gap of GaAs, *n*-type epitaxial layer, $n \approx 10^{15}$ cm⁻³. E_g and $E_{\rm eX}$ indicate the energies of the band gap and free exciton as determined by Sturge [Phys. Rev. <u>127</u>, 768 (1962)]. The peak signal-to-noise ratio is ~100.

ical prediction for $-\Delta \epsilon_1(F, \hbar \omega)$ in the Franz-Keldysh effect at an M_0 edge.^{6,7} We compare with the negative dielectric constant since, as explained later, the laser light decreases the magnitude of the electric field F. We also indicate in Fig. 1 the location of Sturge's⁸ values for the band gap and free-exciton energy. The line shapes shown in Fig. 1 (apart from the sharp spike *B*) are independent of laser intensity; the amplitudes varied approximately as the cube root of the laser intensity.

In Fig. 2 we present the PR spectrum for photon energies near 3 eV, where we find two groups of peaks separated by about 0.23 eV. The locations of these peaks agree with the electroreflectance results⁹⁻¹¹ which have been assigned to spin-orbit-split $\Lambda_3 \rightarrow \Lambda_1$ transitions. Since it is virtually impossible for there to be a significant number of carriers in either the initial or final state, the PR effect cannot be due to band filling, but is most likely due to an electric field associated with the free carriers. It is unlikely that this photoreflectance is actually a thermal effect¹² since the temperature modulation as estimated above is only 0.015° K.

Whereas the structure in Fig. 2 definitely results from an electric field effect, it might be argued that the structure in Fig. 1 does not. There are four data which show that this is very unlikely: (1) The experimental line shape shown in Fig. 1 (except for the sharp spike) is independent of laser intensity. A band-filling effect predicts a line shape dependent upon laser intensity.¹³ (2) The amplitude of the $\Lambda_3 \rightarrow \Lambda_1$ structure follows the same intensity dependence as does the structure in Fig. 1. (3) The experimental line shape near the band gap (Fig. 1) is qualita-



FIG. 2. Photoreflectance spectrum for photon energies near the spin-orbit-split $\Lambda_3 \rightarrow \Lambda_1$ transitions.

tively very similar to the theoretical line shape for the Franz-Keldysh effect^{6,7}; it bears no similarity whatever to the band-filling line shape.² (4) By immersing a p-type sample into an electrolyte, we applied a bias voltage which increased the band bending and surface field. As expected, the strength of the photoreflectance and the spacing of the peaks increased markedly as the bias voltage increased. Thus we conclude that the PR is an electric field effect.

As shown by Hamakawa, Germano, and Handler,⁶ the spacing of the peaks in electroreflectance spectra varies as the electric field is changed. Since we find that the line shape of the PR spectrum is not a function of laser intensity, the field involved cannot arise from a Dember field alone, which would give a field increasing in magnitude with increases in the density of photo excited carriers. The unchanging line shape indicates modulation of a built-in field, i.e., the surface space-charge field. We can estimate the magnitude of the field in the surface depletion region by solving Poisson's equation for a fully ionized donor density of 10^{15} cm⁻³ and a band bending of $\sim 0.5 \text{ eV}$. We find that the surface field is $\sim 10^4$ V/cm. For this field we calculate⁶ that the spacing of peaks in the PR spectrum should be ~8.5 meV. This rough estimate is in very good agreement with the experimental spectrum at 77°K (Fig. 1); at 294°K the spectrum is distorted due to thermal broadening.

Modulation of the surface field could arise from the Dember effect or neutralization of surface space-charge by free carriers. Consider first a modulation by the Dember field. The sign of the Dember field is the same in n-type and p-type material since it depends primarily upon carrier mobilities. However, the built-in field has opposite signs in n-type and p-type samples of GaAs.^{14,15} Thus, the Dember field would increase the magnitude of the field in p-type material but decrease the magnitude of the field in ntype material, and the PR spectra would have opposite signs. On the other hand, the neutralization of the surface field by free carriers is always in a direction which reduces the field. Experimentally we find that the sign of the PR in GaAs is the same in both n-type and p-type samples. Hence, we conclude that PR arises from modulation of the built-in surface field, and the modulation is due to neutralization of surface space-charge by free carriers created by the intense light beam.

The spectral line shape expected from Franz-

Keldysh theory^{6,7} contains a resonant energy equal to the band gap. The experimental resonant energy, which can be estimated from the position of the lowest energy positive peak in Fig. 1 (1.506 eV), is in fact about 8 meV below the band gap and about 5 meV below the energy of the free exciton as determined by Sturge⁸ at 77°K. Sturge's values agree within experimental uncertainty with results of photoluminescence^{16,17} and photoconductivity¹⁸ studies of epitaxial GaAs. Hence, it appears that photoreflectance (and presumably electroreflectance as well) is not simply a band-to-band Franz-Keldysh effect in GaAs. This result is similar to that reported recently for electroreflectance in Ge by Hamakawa, Germano, and Handler,⁶ who concluded that oneelectron theory could not explain their data but that a theory accounting for excitons might do so. Since exciton effects are known to be important in GaAs, they very likely modify the Franz-Keldysh effect and could account for the onset of PR oscillations at energies below the band gap.

The sharp spike labeled B at 1.507 eV in Fig. 1 at 77°K has an intensity dependence different from the rest of the structure. Also note that the width of this spike is much narrower than kT. Hence, its origin differs from that of the rest of the PR spectrum.

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