

Å (at room temperature) measured in experiments with electron excitation. The emitted light is fully polarized in the plane given by the normal of the foil and the direction of observation. The maximum of intensity is obtained if the angle  $\theta$  approaches 25-30° in agreement with Ferrell's calculation and with the electron experiment. The emitted intensity is zero, if one observes in the direction of the foil normal ( $\theta=0$ ). The intensity of the emitted light increases with the thickness of the silver foil and passes through a maximum at a thickness of nearly 300 Å. The intensity maximum shifts to higher frequencies if the foil temperature is decreased, in agreement with the experiments of Arakawa, Davis, and Birkhoff<sup>5</sup> with the silver radiation excited by electrons.

The excitation of the plasma oscillation leads to an additional absorption of the light traversing a thin film of silver, known as plasma resonance absorption, if its frequency equals the plasma frequency  $\omega_p$  and if the electric field vector has a component perpendicular to the foil surface.<sup>6</sup> In the experiment described here the excitation of the plasma mode is observed

by its emitted radiation.

Unpublished measurements of D. Schulz in our institute have shown that the frequency of the plasma resonance absorption (minimum of the intensity of the transmitted, *p*-polarized light<sup>6</sup>) is temperature dependent: Its energy ( $\hbar\omega_p = 3.76 \pm 0.025$  eV  $\Rightarrow \lambda_p = 3280 \pm 20$  Å at room temperature) grows with decreasing temperature as  $\Delta\hbar\omega_p/\Delta T = -3.8 \times 10^{-4}$  eV/deg. This figure is in good agreement with the dependence of the emission peak on temperature excited by electrons or by electromagnetic radiation mentioned above.

<sup>1</sup>R. A. Ferrell, Phys. Rev. 111, 1214 (1958).

<sup>2</sup>W. Steinmann, Phys. Rev. Letters 5, 470 (1960); Z. Physik 163, 92 (1961).

<sup>3</sup>R. W. Brown, P. Wessel, and E. P. Trounson, Phys. Rev. Letters 5, 472 (1960).

<sup>4</sup>E. T. Arakawa, R. J. Herickhoff, and R. D. Birkhoff, Phys. Rev. Letters 12, 319 (1964).

<sup>5</sup>E. T. Arakawa, N. O. Davis, and R. D. Birkhoff, Phys. Rev. 135, A224 (1964).

<sup>6</sup>A. J. McAlister and E. A. Stern, Phys. Rev. 132, 1599 (1963).

## ELECTROREFLECTANCE AT A SEMICONDUCTOR-ELECTROLYTE INTERFACE\*

Kerry L. Shaklee, Fred H. Pollak, and Manuel Cardona

Physics Department, Brown University, Providence, Rhode Island

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We have measured the modulation of the spectral reflectivity by an alternating electric field for several group IV, III-V, and II-VI semiconductors at the interface with an electrolyte. The results are very similar to those obtained recently for germanium, silicon, and GaAs,<sup>1</sup> in which case the electric field is applied by means of a transparent conducting electrode separated from the semiconductor by a thin insulating foil. In addition to its greater simplicity, the electrolyte-semiconductor configuration<sup>2</sup> offers the possibility of extending the measurements of Seraphin and co-workers to shorter wavelengths (the short-wavelength cut-off is determined by the electrolyte and is 1700 Å for water). Modulations in reflectance as high as 0.2% can be obtained with an applied ac voltage of 2 V peak to peak. Furthermore, while accurately flat and smooth samples are required for the transparent-electrode meth-

od, samples obtained by irregular cleavage or fracture can be used for the electrolyte technique. It is also possible to measure samples cleaved within the electrolyte without exposing the surface to air. The transparent-electrode configuration is preferable at low temperatures, but measurements far below 0°C can be performed with the electrolyte method by using suitable low-temperature electrolytes.<sup>3</sup> The electrolyte technique also makes it possible to measure accurately the effects of uniaxial stress. It is also believed that this technique can be used for studying the electrochemistry of semiconductor-electrolyte interfaces.

A dilute solution of KCl in water was used for the room-temperature measurements. A platinum plate was used as one electrode while the other was the material to be measured. The sample was dc biased so as to form a blocking contact and an ac voltage was superimposed

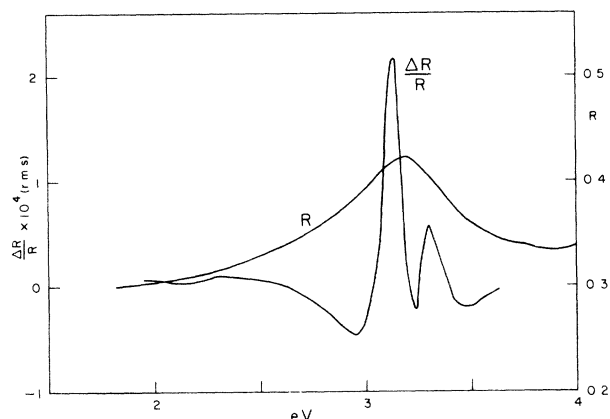


FIG. 1. Reflection and electroreflectance spectrum of InP between 2 and 3.8 eV at room temperature. In agreement with Seraphin's convention,<sup>1</sup>  $\Delta R$  corresponds to a decrease in the applied field at the surface.

onto the bias. In all measurements done the sample had to be negatively biased. The light from a monochromator was reflected from the sample and detected by a photomultiplier. The ac output from the photomultiplier was sent to a lock-in amplifier, and the ratio of the modulated signal to the dc signal was plotted with a recorder. The samples were prepared by polishing and etching or by cleavage. All measurements were performed with unpolarized

light.

The high resolution of the reflectance modulation method, due to derivative feature of the measurement,<sup>1,4</sup> is emphasized in Fig. 1. This figure shows a portion of the room-temperature reflectance spectrum<sup>15</sup> of polycrystalline InP and the corresponding electroreflectance spectrum as obtained by the electrolyte technique. The 3.15-3.31 doublet ( $E_1, E_1 + \Delta_1$  in the standard notation<sup>8</sup>) is not seen in the room-temperature reflectivity, but it is clearly resolved in the electroreflectance spectrum. The value of 0.16 eV, in good agreement with estimates from the low-temperature reflectivity spectrum,<sup>5</sup> is the first reliable value of the spin-orbit splitting reported from InP.

Figure 2 shows the electroreflectance spectra of HgTe, InSb (polycrystalline), GaSb ([111] face), HgSe, and germanium ([110] faces). The peaks associated with the  $E_1$  and  $E_1 + \Delta_1$  transitions are easily identified in HgTe, germanium, and InP. In GaSb, however, two peaks, one positive and one negative, seem to be associated with each one of the  $E_1$  and  $E_1 + \Delta_1$  transitions. Seraphin<sup>1</sup> has made similar observation for GaAs and has suggested that the higher energy component of the two peaks associated with each transition is the one which corresponds to the singular energy gap. Follow-

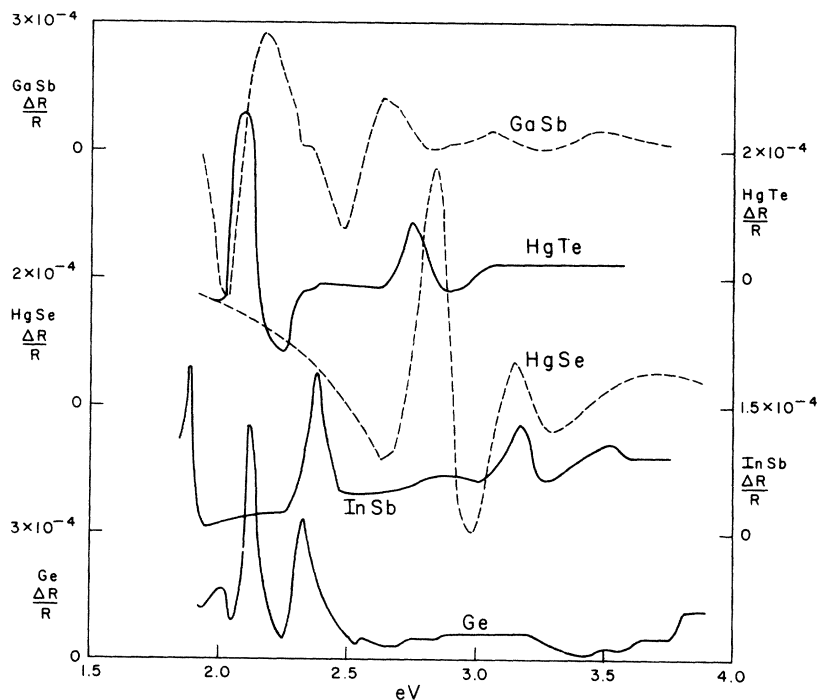


FIG. 2. Electroreflectance spectra of germanium, InSb, GaSb, GaAs, HgTe, and HgSe between 1.8 and 3.8 eV at room temperature.

Table I. Energies of the  $E_1$  and  $E_1 + \Delta_1$  peaks as observed in the electroreflectance, absorption, and reflection spectra at room temperature.

		Ge	InSb	GaSb	GaAs	InP	HgTe	HgSe
$E_1$	Electroreflectance	2.115	1.895	2.185	2.96 <sup>a</sup>	3.150	2.110	2.845
	Absorption	2.15	1.89	2.07	2.97		2.14	2.87
	Reflection	2.10	1.83	2.02	2.94	3.15	2.09	2.82
$E_1 + \Delta_1$	Electroreflectance	2.325	2.385	2.655	3.20 <sup>a</sup>	3.31	2.760	3.160
	Absorption	2.35	2.44	2.56	3.2		2.78	3.20
	Reflection	2.30	2.35	2.48	3.13	3.3	2.71	3.13

<sup>a</sup>See B. O. Seraphin, Phys. Rev. 140, A1716 (1965).

ing this convention, we have listed in Table I the room-temperature positions of the  $E_1$  and  $E_1 + \Delta_1$  gaps observed by electroreflectance in GaAs, GaSb, and the other materials measured. We have also listed the position of the peaks observed in the room-temperature absorption and reflection.<sup>6,7</sup> Since these peaks are caused by an  $M_1$  singularity in the density of states, the peak in absorption should occur at the energy of the corresponding gap. The peaks in reflectance occur at slightly lower energies, as expected. For all materials measured, with the exception of GaSb, the electroreflectance peaks listed in Table I fall between the corresponding absorption and reflection peaks. Both the  $E_1$  and the  $E_1 + \Delta_1$  peaks of GaSb occur at energies 0.1 eV higher than the corresponding absorption peaks. This shift is too high to be due to lattice defects and its cause is not known at present.

Besides the  $E_1, E_1 + \Delta_1$  doublet, additional structure is apparent in several of the curves of Fig. 2. In particular, for germanium, structure is seen around 3.5 eV attributed to the  $E_0'$  transitions.<sup>1</sup> Also, the peak seen around 2 eV could be due to the  $\epsilon_1$  transitions at the  $L$  point ( $L_3' - L_1$ ). Structure possibly due to the  $\epsilon_1$  transitions is seen at 2 eV in HgTe. The weak structure around 2.4 eV in HgTe and 2.12

eV in InSb could be due to the  $\epsilon_1 + \Delta_1$  transitions. Finally, oscillations are seen above 2.8 eV in GaSb and at 3.17 and 3.52 eV in InSb. This last peak of InSb is probably associated with the  $E_0'$  transitions. The fine structure of these spectra will be discussed in detail elsewhere.

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<sup>1</sup>B. O. Seraphin and R. B. Hess, Phys. Rev. Letters 14, 138 (1965); B. O. Seraphin and N. Bottka, Phys. Rev. Letters 15, 104 (1965); B. O. Seraphin, Phys. Rev. 140, A1716 (1965).

<sup>2</sup>R. Williams, Phys. Rev. 117, 1487 (1960).

<sup>3</sup>Propyl alcohol could be used down to  $-127^\circ\text{C}$ .

<sup>4</sup>A derivative method has been also used for piezoreflectance measurements [see W. E. Engeler, H. Fritzsche, M. Garfinkel, and J. J. Tiemann, Phys. Rev. Letters 14, 1069 (1965); G. W. Gobeli and E. O. Kane, Phys. Rev. Letters 15, 142 (1965)], but the resolution obtained in piezoreflectance does not seem as high as that in electroreflectance.

<sup>5</sup>M. Cardona, J. Appl. Phys. 32, 958 (1961).

<sup>6</sup>This doublet is believed due to direct transition at a  $\vec{k}$  point in the [111] direction inside the Brillouin zone [see M. Cardona, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod, Paris, 1964), p. 181].

<sup>7</sup>M. Cardona and G. Harbeke, J. Appl. Phys. 34, 813 (1963).