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DIRECT AND WAVELENGTH MODULATED PHOTOCONDUCTIVITY AND
PHOTOVOLTAIC EXCITATION SPECTRA OF CuGaS$_2$

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Résumé. — On a étudié la distribution spectrale de la photoconductivité et principalement celle de l’effet photovoltaïque — sans ou avec modulation de longueur d’onde — sur une barrière de Schottky Au-CuGaS$_2$ à 300 K et 90 K. Les spectres révèlent, aux énergies supérieures et inférieures à celle de la bande interdite, plusieurs structures pouvant être reliées aux structures dans les spectres d’absorption, de réflectivité et de luminescence. La présence de pièges à électrons profonds est également révélée. Le transfert d’électrons, sous excitation optique, d’accepteurs compensés vers ces pièges provoque une augmentation de la conductivité et de la photosensibilité.

Abstract. — The spectral distribution of the photoconductivity and, principally, of the photovoltaic and wavelength modulated photovoltaic effect for a Au-CuGaS$_2$ Schottky barrier, has been studied at 300 K and 90 K. Several structures are observed in the spectra at energies above and below the gap, which can be related to absorption reflectivity or luminescence structures in the material. The presence of deep electron traps is also revealed. The transfer of electrons under optical excitation, from compensated acceptors to these traps enhances the dark conductivity at low temperatures and has a sensitizing effect on the photoconductivity.

1. Introduction. — The new ternary materials CuGaS$_2$ and CuInS$_2$ have recently been the subject of interest for their semiconducting and optical properties in view of their possible applications in nonlinear optics [1], [2], [3] and electroluminescent diodes [4], [5], [6]. Optical absorption [5], [7], [8], [9], [10], reflectivity [5], [7], [8], [9], [10] and luminescence [11] have been investigated for CuGaS$_2$. Recently Tell and al. [12] have studied the structure of the valence band of the compounds by alloying them in the form of CuGa$_{1-\alpha}$In$_\alpha$S$_2$.

Recent efforts to investigate the low temperature photoconductivity of CuGaS$_2$ have met with difficulties related to photomemory effects and to the non-reproducibility of results. PEM effect studies are also likely to be difficult because of the low carrier mobility in the material. We present here some preliminary results on the photoconductivity at 300 K and on the photovoltaic and wavelength modulated photovoltaic effects at a Au-CuGaS$_2$ Schottky barrier at 300 K and 90 K. Some structures seen in absorption or reflectivity are also observed in the PV spectra and mostly in their derivatives. This method of observation is relatively simple; the signal is strong and the results are reproducible and less sensitive to many of the extrinsic effects seen in photoconductivity and even in luminescence.

2. Experimental. — The samples of a few mm$^2 \times 1$ mm were of the orange variety (undoped) with natural (112) faces. Contacts were made in the sandwich configuration, the ohmic back contact consisting of aquadag (colloidal graphite) and the front rectifying contact consisting of a semi-transparent evaporated gold layer. The material was semi-insulating with a resistivity of about $10^6 \Omega\cdot$cm at room temperature. The samples were mounted stress-free with General Electric DC-Z9 compound in a cryostat equipped with an independent experimental chamber and good thermal contact was provided by a He exchange gas at a pressure of about 1 torr. The optical system consisted of a ½ meter spectrometer equipped with a vibrating refractor plate (12 Hz) located near the entrance slit and producing a modulation amplitude of about 10 Å. For A. C. measurements (light intensity modulation) light was chopped at 85 Hz and synchronous detection used with the electrometer at unity gain serving as a high to low impe-
dance transformer. The D. C. measurements (constant illumination) were made with a high impedance electrometer.

The P. C. and P. V. spectra were obtained under unpolarized illumination. All P. V. spectra were recorded at zero bias since during a test run, external bias of up to one volt showed no significant influence on the results.

3. Preliminary remarks on P. C. and P. V. detectors. —

3.1 P. C. DETECTOR. — The photoconductivity in a semi-conductor in the intrinsic range may be a combined majority and minority carrier effect. Moreover the lifetimes of the photocarriers depend strongly on the actual population of the recombination centers or traps. Thus if during illumination a charge exchange occurs between two types of centers these parameters may be modified. Another difficulty may arise from electrode effects if the contacts are not strictly ohmic.

3.2 P. V. DETECTOR. — The P. V. effect is in principle essentially a minority carrier effect (electrons in the case of CuGaS₂) phenomenon. This is known to be true for low resistivity materials, but can also be easily demonstrated for high resistivity materials [13]. On the other hand owing to the strong electric field in the barrier, electrons tend to remain in it for a period substantially shorter than their mean lifetime. Consequently no recombination occurs in the effective photocell space and all electrons generated in the barrier region will contribute to the P. V. effect. Thus the P. V. effect appears to be less sensitive to extrinsic effects than the photoconductivity. For low values of the optical absorption coefficient \( \alpha \) with respect to the width \( W \) (generally of the order of \( 10^{-6} \) to \( 10^{-4} \) cm) of the barrier (\( \alpha^{-1} > W \)) only a fraction proportional to \( \alpha \) of the incident photons is absorbed. For high values of \( \alpha \) (\( \alpha^{-1} < W \)) the P. V. effect is governed only by the total amount of light energy penetrating into the sample. Thus if the incident photon flux is independent of wavelength, the spectral response will be proportional to \( \alpha \) in the low energy region (provided that free carriers only are created) and show a saturation in the high energy region which begins at a wavelength which satisfies approximately the condition \( \alpha^{-1} \approx W \). However reflectivity anomalies resulting in the effective photon flux penetrating into the sample may well be detected in this region especially in the wavelength modulated spectrum.

4. Results and discussion. —

4.1 Photoconductivity at 300 K. — Photoconductivity spectra at 300 K present no particular problems. Such a spectrum is shown in figure 1 in both direct and wavelength modulated forms. The high energy maximum at 0.501 \( \mu \)m (2.48 eV) can be attributed to band to band transitions. This value found for the band gap is in good agreement with the one deduced from optical measurements. The low energy peak at about 0.516 \( \mu \)m seems to correspond to:

a) the electroluminescence band at 0.518 \( \mu \)m observed at room temperature by Wagner et alii [14];

b) the luminescence peak in the interval 0.5165 - 0.519 \( \mu \)m, observed by J. von Bardeleben et alii [11] at low temperature;

c) the absorption line at 0.513 \( \mu \)m (2.416 eV) observed at 4.2 K by Ringelissen et alii [9], Regolini [10] and Regolini et alii [8] in green crystals.

The absorption band has been attributed to impurity centers. However, it has not been observed in the spectrum of orange crystals, probably because the concentration of impurity absorbers is too low in this type of material. J. von Bardeleben et alii attribute the corresponding luminescence band (which is also present in the spectrum of undoped, i.e. orange crystals) to donor-acceptor recombinations. The absorption at 0.513 \( \mu \)m may thus correspond to valence band-donor transitions. This correlation allows to estimate the donor ionization energy at about 80 meV. Taking into account the value 160 meV obtained by J. von Bardeleben et alii for \( E_d + E_A \) (\( E_d \) = acceptor and \( E_A \) = donor ionization energy respectively), a weaker absorption band corresponding to acceptor-donor transitions may be expected to lie at about 0.525 \( \mu \)m (2.36 eV). So far, no absorption as well as no structure in the photoconductivity spectrum could be detected in this wavelength region.

The importance of the extrinsic peak compared to the intrinsic photoconductivity leads to the conclusion that the lifetime of the holes created in the bulk of the material by extrinsic excitation is very high with respect to the lifetime of the photocarriers generated near the surface by the strongly absorbed intrinsic excitation.

Optical excitation may also be coupled with a shift of the Fermi level towards the valence band. Such a shift gives rise to a strong increase in conduc-
Activity which may remain for a more or less long time after the light has been removed; however, it needs an appreciable charge transfer from ionized acceptors to deep electron traps and consequently it is more likely to occur at low temperatures. Indeed as the temperature is lowered the P. C. signal in the extrinsic region becomes very high and the spectra are very difficult to reproduce because of photomemory effects: the light induces a strong enhancement of the dark conductivity which depends on the light intensity and on the exposure time and simultaneously an increase of the photosensitivity is observed. The decrease of the conductivity after interruption of the illumination is a very slow process. These preliminary observations indicate the presence of deep electron traps in CuGaS$_2$. As a result of illumination, electrons are transferred from compensated acceptor centers to these traps. The charge exchange has a sensitizing effect on photoconductivity. If the temperature is sufficiently low, the non-equilibrium state may exist for an indefinite time after illumination.

Thus the simple but classical photoconductivity measuring technique could not give meaningful results. For this reason no further attempt was made to record low temperature P. C. spectra.

4.2 PHOTOVOLTAIC EFFECT AT 300 K. — In principle, for the reasons invoked above the P. V. spectra should be less sensitive to extrinsic effects. A typical direct (intensity modulated) spectrum is shown in figure 2. This spectrum exhibits, in general, a single structure. In all cases it drops off more sharply than the P. C. spectrum, in the low energy range. The reason is that the signal measured by the P. V. detector depends mainly on the absorption coefficient $\alpha$, thus extrinsic absorption, which is weak compared to intrinsic absorption in orange CuGaS$_2$, can hardly be detected. For the same reason the P. V. response decreases more slowly in the high energy range than the corresponding P. C. signal.

The observed decrease reflects in fact the variation of the photon flux transmitted by the optical system. Sometimes the P. V. spectrum exhibits a double structure as shown in figures 3 (intensity modulated) and 4 (wavelength modulated). This structure seems to correspond to an electroreflectance structure ($D_2$) observed by Tell et alii [4] at 300 K for $E \perp Z$ near 0.492 $\mu$m (2.52 eV). It is possible that the high electric field in the barrier induces a kind of electroreflectance. The fact that no corresponding structure could be observed in the P. C. spectrum is an argument in favour of the proposed interpretation.

**FIG. 3.** — Photovoltaic effect as a function of wavelength at 300 K (intensity modulated).

**FIG. 4.** — Derivative of the spectral response curve of the photovoltaic effect at 300 K.
4.3 PHOTOVOLTAIC EFFECT AT 90 K. — At 90 K a P. V. excitation spectrum can still be obtained but of a completely different shape (Fig. 2). A peak appears at 0.49 μm in the intensity modulated spectrum. At longer wavelengths however the signal becomes negative indicating either a phase reversal or a sign reversal of the photovoltage.

A sign reversal can be ruled out because it should be attributed only to the inversion of the electric field in the Au-CuGaS₂ barrier i.e. to the conversion of the conductivity from p- to n-type.

The λ-derivative spectrum, obtained at a lower modulation frequency, shows two well defined structures, but because of a possible wavelength dependent phase difference between the P. V. response and the excitation its interpretation is somewhat doubtful. Figure 5 shows a comparison between the derivative spectra of the P. V. effect and of the reflectivity which have been recorded simultaneously at 90 K. The latter curve is very similar to the one obtained by Ringeissen et alii [9] in the $E \perp Z$ configuration. The largest negative peak of $\Delta R/R$ at 0.496 μm (2.50 eV) corresponds to the $n = 1$ exciton line [8], [9], [10]. The negative peak in the modulated reflectivity is generally taken as the significant position as far as transitions are concerned; it is interesting to note that its position corresponds to the inflection point of the corresponding peak in the λ-modulated P. V. spectrum.

Tell et alii [4] and Ringeissen [9] and Regolini et alii [8], [10] reported a reflection anomaly near 2.626 eV (0.472 μm). This anomaly is also visible in both spectra on figure 5 as well as on figure 4.

4.4 P. V. RESPONSE UNDER CONTINUOUS ILLUMINATION. — Figure 6 shows a P. V. spectrum obtained at about 90 K under continuous illumination. This curve exhibits a completely different form than the one obtained under intensity modulated illumination.

First it is interesting to note that in the whole spectral range the photovoltage has the same polarity, thus it can be concluded that when the excitation intensity is modulated, even at low frequency, some slow relaxation effects lead to a wavelength dependent phase difference.

The general shape of the curve also contradicts the normal behaviour of a P. V. detector: indeed the signal is larger in the low energy range ($0.485 \mu m < \lambda < 0.52 \mu m$) than in the high energy range ($\lambda < 0.483 \mu m$).

In order to explain the origin of these unusual observations one has to keep in mind the working of a P. V. detector. The P. V. effect is frequently analysed in terms of an equivalent circuit including an external load resistance $R_L$ [15] (Fig. 7). The effect of radiation is represented by a constant current generator $i_s$; $Z$ is a non-linear impedance; $R_s$ is the shunt resistance; thus it can be concluded that when the excitation intensity is modulated, even at low frequency, some slow relaxation effects lead to a wavelength dependent phase difference.
tance of the barrier layer, \( R_s \) is the resistance of the body of the sample and \( V_{PV} \) is the photovoltage. If the cell is open circuited \( (R_s = \infty) \) a voltage \( V_{PV} \) is built up just sufficient to counterbalance the current flow \( i_s \), thus one has

\[
i_s = i_r \quad \text{and} \quad i_s = 0.
\]

If on the contrary the cell is short-circuited i. e. \( R_s \ll R_p \) and \( R_L \ll R_p \), then \( V_p = 0 \) and \( i_r = 0 \) and \( i_L = i_r \).

Under practical circumstances one has an intermediate situation. For simplicity the assumption is made that the condition \( R_s \ll R_p \) is always satisfied. The shunt resistance \( R_s \) may of course be changed by the incident radiation, below a certain temperature when the density of free photocarriers in the layer becomes higher than the density of carriers present in the dark, but it is plausible to assume that the effect on \( R_s \) will be small because the lifetime of the photocarriers in the barrier is mainly limited by the short transit time rather than by the recombination time.

As long as the incident radiation is strongly absorbed \(-\alpha^{-1}\) much smaller than the thickness of the sample \( R_s \) is not appreciably affected and the P. V. cell exhibits a normal behaviour. Such a situation holds for the high energy section \((\lambda < 0.485 \mu m)\) of the curve of figure 6. When the absorption becomes lower, so that it takes place in the whole sample, \( R_s \) may be strongly decreased, if the lifetime of the photocarriers is much longer than the transit time of those carriers which are generated in the barrier. Consequently in the circuit of figure 7 better short circuit conditions are realized and the measured signal \( i_L \) increases although less photons are absorbed in the rectifying layer. When the absorption becomes too weak (i. e. \( i_s \) small) the P. V. signal drops off again very sharply \((\lambda > 0.51 \mu m)\).

The slow relaxation effects, which lead to the wavelength dependence of the phase difference between the P. V. signal and the excitation can thus be attributed to the bulk photoconductivity of the sample.

Finally it is interesting to note that the structures seen at 0.496 \( \mu m \) and 0.5008 \( \mu m \) correspond to the \( n = 1 \) free exciton line and to a bound exciton line respectively \([8],[9],[10]\).

It would be interesting to record P. V. spectra at temperatures lower than 90 K. However below 90 K the P. V. signal goes down steadily and it becomes impossible to detect since the sample is now highly insulating \((R_s \gg R_p)\).

5. Conclusion. — The above preliminary results indicate that photoeffects and mainly their \( \lambda \)-derivative spectra can be used to give information on the optical properties of CuGaS\(_2\), at least in some temperature range. If this range can be lowered, it may be possible to study interband magneto-optical effects with moderate field values since the effective masses are believed to be in the 0.1 to 0.2 \( m_0 \) range. This study could then be done with relative ease by the P. V. effect technique, which appears to be the most interesting tool and which has been highly successful in Ge \([16]\) and InP \([17]\). In order to use this technique at low temperatures for the study of CuGaS\(_2\) either thick samples which much higher electrical conductivity or better thin samples of high conducting trap free material will have to be used.

References