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Trapping Phenomena in Iron-doped $GaAs_{0.5}P_{0.5}$

by **H. Schade**

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(6. V. 68)

Abstract. Trapping parameters have been determined from measurements of thermally stimulated conductivity and space charge limited currents in a vapor-phase-grown sample of semi-insulating, iron-doped $GaAs_{0.5}P_{0.5}$. From an analysis of the data it follows that there is a distinct trapping level at 0.61 eV above the valence band. It is shown that the associated trap densities deduced from both kinds of measurement refer to centers of different charge. The thermally stimulated conductivity measurement yields the equilibrium concentration $N_{no} \cong 2 \times 10^{15}$ cm^{-3} of the *ionized* acceptors. The space charge limited current measurements are consistently explained on the basis of a model by Ashley and Milnes, assuming double injection with trapping. According to this model the lifetime of the electrons is determined, which in turn yields the equilibrium concentration $N_{po} \cong 2 \times 10^{14}$ cm^{-3} of the *neutral* acceptors. According to the same model the concentration of the neutral acceptors decreases with increasing voltage. The voltage for which the supply of neutral centers becomes exhausted is calculated and agrees with the voltage at which the onset of breakdown is observed. It is concluded, therefore, that the breakdown is due to the exhaustion of electron-capturing centers.

I. Introduction

The electrical properties of photoconductors are essentially determined by the energy and concentration of the trapping centers. Studying these parameters is especially suitable in high-resistivity Ga(As-P) alloys which may be prepared in a well-controlled manner by a vapor growth technique [1, 2]. Two widely used methods to determine these trapping parameters are measurements of thermally stimulated

currents and space-charge limited currents [3]. However, the corresponding values obtained by these two methods are frequently not in agreement [4]. It is the purpose of this study not only to determine trapping levels in iron-doped $GaAs_{0.5}P_{0.5}$, but also to compare results which are deduced from measurements of thermally stimulated conductivity and of space charge limited currents in one and the same sample of $GaAs_{0.5}P_{0.5}$.

The bandgap of $GaAs_{0.5}P_{0.5}$ at room temperature is 1.95 eV [1]. Semi-insulating properties result from compensation of normally present donor centers by incorporating iron during crystal growth. Iron forms deep acceptor states in Ga(As-P) alloys; the compensation yields p-type conductivity [2, 5]. Evidence for p-type conductivity in the present sample has been provided by R. WILLIAMS [6] who inferred from open circuit photo-voltage measurements that the Fermi level must be located at least 1.0 eV below the conduction band.

II. Experimental Details

The sample was a special type of diode consisting of a vapor-grown epitaxial layer of $GaAs_{0.5}P_{0.5}$ (thickness $L \cong 2 \times 10^{-3}$ cm) on a n-type GaAs substrate. An ohmic contact was made to the low resistivity GaAs substrate, and an electron blocking contact (contact area $A \cong 2.5 \times 10^{-2}$ cm^2) was prepared on top of the epitaxial layer by evaporation of gold. The corresponding energy band diagram of the sample is shown in Figure 1. Note that the p-n junction lies wholly within the $GaAs_{0.5}P_{0.5}$, and not at the heterojunction.

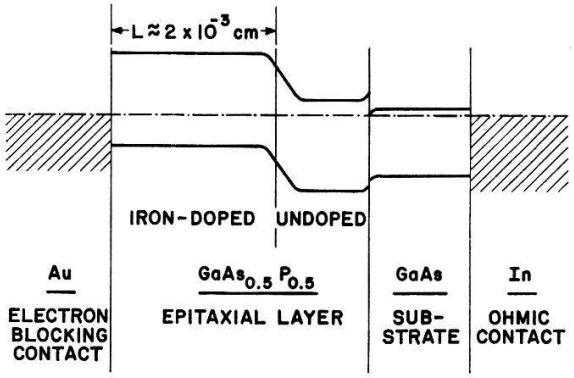

Figure 1

Schematic energy band diagram of III–V alloy structure.

The electrical measurements were performed in a conventional *dc* apparatus consisting essentially of a stabilized power supply and a sensitive electrometer. Thermally stimulated conductivity was measured after the sample had been illuminated by a low pressure mercury arc lamp or by a tungsten lamp for 5 minutes at liquid nitrogen temperature. For both kinds of excitation the infrared parts of the spectrum were cut off using Corning filters 1–69 (transmitting $h\nu > 1.25$ eV). The energy of light incident on the sample was measured with a calibrated thermopile. The temperature was varied in the range from 90 to 350 °K. The heating speeds during the thermal stimulation of carriers were constant (0.34 or 0.79 deg/sec).

III. Results and Discussion

A. *Thermally Stimulated Conductivity*

Thermally stimulated conductivity has been measured under reverse bias of 10 V (Au-electrode negative, GaAs substrate positive) and is shown in Figure 2. The sample had been cooled down to 90 °K in the dark with no bias applied and illuminated. The experimental results are the same for both kinds of excitation (using the mercury or tungsten lamp). There is a distinct conductivity peak at 207 °K. Further stimulation of conductivity, though not yielding a well-defined conductivity peak, occurs in the temperature range between 110 and 150 °K.

A similar behavior of stimulated conductivity is found if, instead of using optical excitation, the traps are filled by injection of excess carriers. This is achieved by cooling down the sample in the dark under a forward bias of the order of 10 V (Au-electrode positive, GaAs substrate negative). Thermally stimulated conductivity is then measured under reverse bias. In this case the well-defined peak at 207 °K appears again in the same order of magnitude as after excitation by light, whereas the stimulated conductivity between 110 and 150 °K is about 2 orders of magnitude smaller (see Fig. 2).

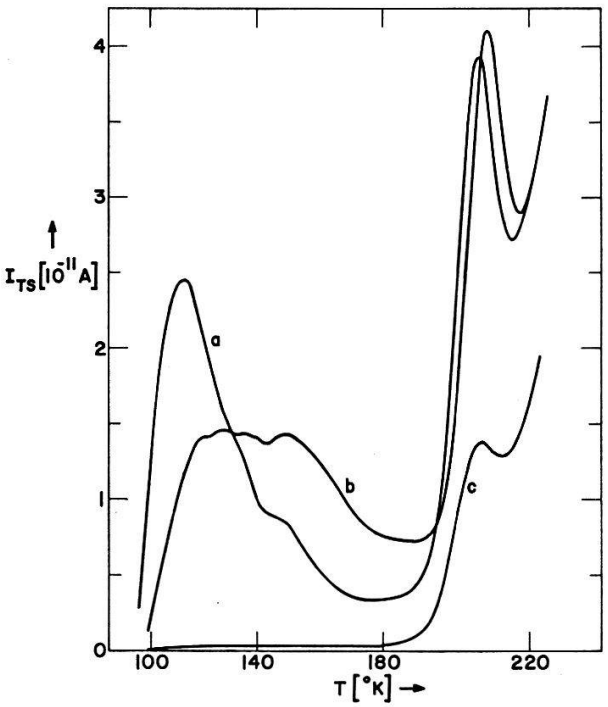

Figure 2

Thermally stimulated currents in $GaAs_{0.5}P_{0.5}$ structure under reverse bias of 10 V a) and b) after excitation by light c) after excitation by carrier injection.

1. Concentration of Trapped Carriers

The concentration of trapped carriers is given by [7]:

$$N_t = \frac{A_t}{e\,V\,G} \tag{1}$$

where A_t is the total charge released from the respective trap, V is the effective volume of the crystal, G is the photoelectric gain, and e is the elementary charge.

The effective volume of the crystal is the volume in which excess carriers generated by light of a certain spectral distribution have been trapped. For the geometry of the sample and the spectral distribution used, the volume is equal to the area A of the gold contact multiplied by the thickness L of the epitaxial layer of the $GaAs_{0.5}P_{0.5}$. The maximum intensities of the light using infrared filters (Corning 1–69) occur at 2.22 eV for the mercury lamp and at 2.06 eV for the tungsten lamp. The corresponding reciprocal absorption constants have the same order of magnitude [8] as the thickness $L \cong 2 \times 10^{-3}$ cm.

The photoelectric gains have been measured at 207 and at 120 °K, using mercury and tungsten light. The following values refer to steady state photocurrents which were adjusted by neutral density filters to be equal to average values of the corresponding thermally stimulated current peaks: G (120 °K) $= 1.8 \times 10^{-1}$ and G (207 °K) $= 3.2 \times 10^{-2}$ for mercury light; G (120 °K) $= 2.5 \times 10^{-2}$ and G (207 °K) $= 1.1 \times 10^{-2}$ for tungsten light.

From Equation (1) it follows that the conductivity peak at 207 °K corresponds to the trap density $N_t \cong 2 \times 10^{15}$ cm^{-3} (mercury light excitation $N_t = 1.1 \times 10^{15}$ cm^{-3}, tungsten light excitation $N_t = 3.5 \times 10^{15}$ cm^{-3}).

The stimulation of conductivity over a rather wide temperature range between 110 and 150 °K indicates a quasi-continuous distribution of trapping levels around a certain energy (see below). Since the distribution of these traps varies for different runs, as shown in Figure 2, it may be due to surface or interface effects. The total number of these traps deduced from the photoelectric gain G (120 °K) and the total charge A_t released in the temperature range between 110 and 150 °K is not more than 10^{11}, which corresponds either to a volume concentration of not more than 2×10^{15} cm^{-3} or to a surface concentration of not more than 4×10^{12} cm^{-2}.

2. Energy of Trapping Levels

The energy of an electron (hole) trap measured from the conduction (valence) band is given by [9]:

$$|E_t - E_{c,v}| = k\, T_m \ln \left[\frac{e\, \mu_{n,p}\, N_{c,v}}{\sigma_m}\right] \tag{2}$$

where E_t is the energy of the trap level, $E_{c,v}$ is the energy of the bottom (top) of the conduction (valence) band, T_m is the temperature at which the conductivity maximum occurs, σ_m is the conductivity at T_m, $\mu_{n,p}$ is the electron (hole) mobility at T_m and $N_{c,v}$ is the effective density of states in the conduction (valence) band.

Assuming $N_c = N_v = 10^{19}$ cm^{-3} and either taking μ_n (207 °K) $= 10^3$ cm^2/Vsec or μ_p (207 °K) $= 10^2$ cm^2/Vsec[1]), the conductivity peak at 207 °K corresponds respectively to an electron trap at $E_c - E_t = 36\, k\, T_m = 0.65$ eV below the conduction band, or to a hole trap at $E_t - E_v = 34\, k\, T_m = 0.61$ eV above the valence band. A decision as to whether an electron or a hole trap is involved follows from an analysis of the forward characteristic given in the following section; a thermally stimulated Hall effect measurement could not be performed with the geometry of the sample used.

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[1]) Both mobilities are assumed to vary with temperature roughly similar to GaP [10, 11] as $\mu_n \sim T^{-1.9}$ and as $\mu_p \sim T^{-1.5}$. The room temperature value of the electron mobility is assumed to be $\mu_n = 500$ cm^2/Vsec [12], and that of the hole mobility is assumed to be equal to the value $\mu_p = 60$ cm^2/Vsec in GaP [11].

The energy of the trapping levels corresponding to the stimulated conductivity in the temperature range between 110 and 150 °K is 0.35 to 0.45 eV measured from either band edge. These levels will not further be discussed, since, as mentioned, they might not represent bulk properties.

B. *Current-voltage Characteristic*

1. Dark Conductivity (Reverse Bias)

Under reverse bias (Au electrode negative, GaAs substrate positive) the current voltage characteristic is ohmic up to 300 V [6] (see Fig. 3); the dark conductivity is determined by the equilibrium density of the holes in the $GaAs_{0.5}P_{0.5}$ layer. As shown in Figure 4, the temperature dependence of the dark conductivity is exponential, showing an activation energy of $E_{Fo} - E_v = 0.68$ eV. This energy approximately corresponds to the energy difference between the equilibrium Fermi level E_{Fo} and the top of the valence band E_v. Using the room temperature conductivity of $\sigma = 2 \times 10^{-10}\ (\Omega\text{cm})^{-1}$, the energy $E_{Fo} - E_v = 0.68$ eV, and assuming an effective density of states in the valence band $N_v = 10^{19}\ \text{cm}^{-3}$, one obtains the room temperature value of the hole mobility $\mu_p = 40\ \text{cm}^2/\text{Vsec}$, which is in reasonable agreement with the assumed value.

2. Space Charge Limited Currents (Forward Bias)

The forward characteristic (Au electrode positive, GaAs substrate negative) is non-linear, as shown in Figure 3. After an ohmic portion at low voltages, the current rises strongly at about 1 V. This rise corresponds to the increasing injection of electrons from the GaAs substrate due to the decrease of the potential barrier for electrons

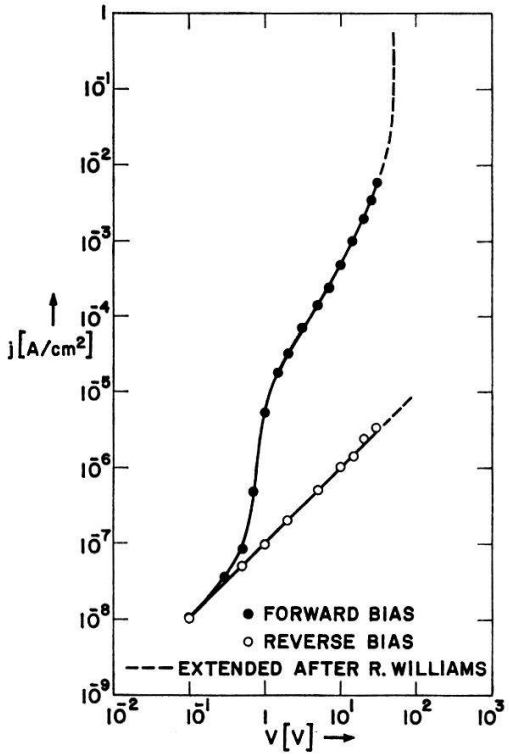

Figure 3

Current voltage characteristic of $GaAs_{0.5}P_{0.5}$ structure at room temperature.

between the n-type and p-type portions of the sample. In the range from 2 to 20 V the current is proportional to V^2, indicating space charge limitation. The strong increase in current at about 50 V, measured by WILLIAMS [6], may be due to a trap filled limit or to double injection (see below). The temperature dependence of the forward current is also exponential, as shown in Figure 4. The activation energy is independent of the applied forward bias up to about 15 V (0.65 eV for 5 V, 0.68 eV for 10 V) and has nearly the same value as the activation energy for reverse bias.

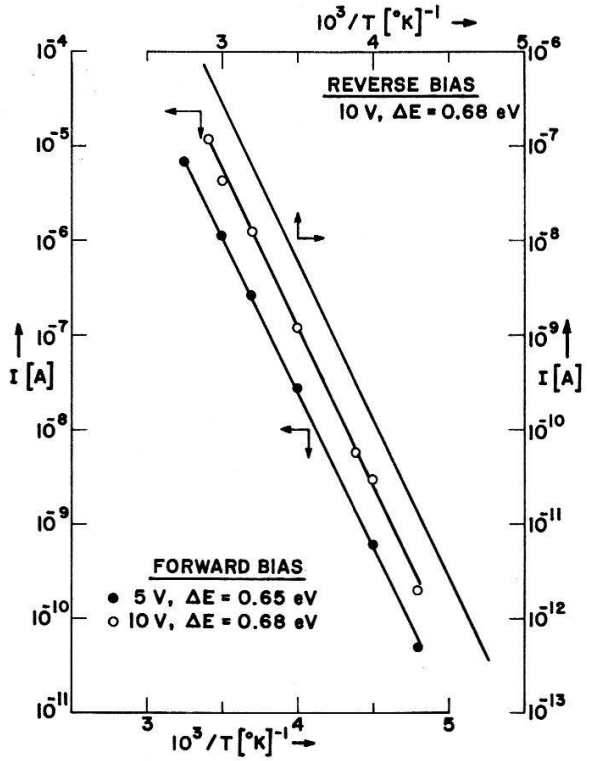

Figure 4

Temperature dependences of forward and reverse currents in $GaAs_{0.5}P_{0.5}$ structure.

3. Analysis of the Forward Characteristic

The current voltage characteristic due to the injection of carriers into a semiconductor is strongly influenced by the concentration and energy of trapping states [13]. Assuming a one carrier model and assuming that the traps present are at least several $k\,T$ above the Fermi level ($E_t - E_{Fo} \gg k\,T$), their number and energy may be obtained from the temperature dependence of the square law portion of the forward characteristic [4, 13]. The results of this analysis are to be compared with the results from the thermally stimulated conductivity measurements. If the thermally stimulated conductivity peak at 207 °K is due to an electron trap, its energy position at $E_c - E_t = 0.65$ eV is indeed several $k\,T$ above the Fermi level at $E_{Fo} - E_v = 0.68$ eV. The temperature dependence of the square law portion of the forward characteristic, however, yields a trap concentration which would be 3 orders of magnitude smaller than N_t determined from the stimulated conductivity. Since this would be unreasonably small, it is concluded that the forward characteristic is not adequately described by a one carrier model.

Instead, if the conductivity peak at 207 °K is due to a hole trap at $E_t - E_v = 0.61$ eV, the forward characteristic has to be explained by a two carrier model (double injection). There are two reasons: (1) the trap level at 0.61 eV above the valence band is deep with respect to the Fermi level, and a one carrier model with deep traps would yield an ohmic current-voltage characteristic [13] instead of the observed square law. (2) The conductivity peak at 207 °K also occurs after excitation of carriers by the application of a forward bias (see Fig. 2), and it is considered to be due to the same hole trap as that filled by light excitation.

Double injection with trapping has been studied by ASHLEY and MILNES [14], and their model proves to be consistent with our experimental results. According to this model, a single set of recombination centers governs the capture and recombination of injected carriers under forward bias conditions. We assume that the recombination centers are acceptor-like, and that their energy position and equilibrium occupation is given by the thermally stimulated conductivity measurement: $E_t - E_v = 0.61$ eV and $N_t = N_{no} = 2 \times 10^{15}\,\mathrm{cm}^{-3}$. Because the Fermi level lies above the acceptor level ($E_{Fo} - E_v = 0.68$ eV and $E_t - E_v = 0.61$ eV), the equilibrium concentration N_{po} of the unoccupied (neutral) centers is much smaller than N_{no}, the total concentration of acceptor centers being $N_R = N_{no} + N_{po}$ (see Fig. 5). Since the material is partly compensated, there has to be a concentration of about N_{no} shallow donors. These are considered to play no further role in the observed electrical properties of the specimen.

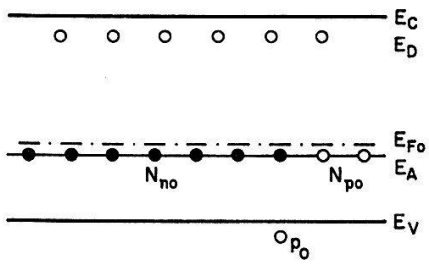

Figure 5

Assumed energy band diagram of semi-insulating $GaAs_{0.5}P_{0.5}$.

The cross section S_p for capture of holes by the occupied (negatively charged) acceptor centers is assumed to be much greater than the cross section S_n for electrons by the unoccupied (neutral) acceptor centers: $S_p \gg S_n$. Under this assumption the forward current-voltage characteristic is given by [14]:

$$I = \frac{9}{8} \frac{\tau_n}{\tau_{p\Omega}} \varepsilon\, \varepsilon_0\, \mu_n \frac{V^2}{L^3} \tag{3}$$

with

$$\tau_{p\Omega} = \frac{\varepsilon\, \varepsilon_0}{\sigma} \tag{4}$$

where the following notation is used: current density I, forward bias V, electron lifetime τ_n, dielectric relaxation time $\tau_{p\Omega}$ due to the equilibrium holes, electron mobility μ_n, permittivity constant ε_o, dielectric constant ε, equilibrium conductivity σ. A characteristic feature of Equation (3) is the temperature dependence of the current, which is essentially determined by the exponential temperature dependence of the

equilibrium hole concentration (assuming τ_n and μ_n to be only slightly temperature dependent with respect to the exponential temperature dependence of σ). There is satisfying experimental agreement for this behavior; the temperature dependence of the forward current is exponential, as shown in Figure 4, and the activation energy is nearly independent of the applied forward bias and equal to the activation energy of the dark conductivity (0.65 eV for 5 V, 0.68 eV for 10 V).

The essential quantity of Equation (3) is the lifetime of the electrons, which is related to the concentration of the electron capturing centers by the relation:

$$\tau_n = \frac{1}{v\, S_n\, N_{po}} \tag{5}$$

where $v = (2\, k\, T/m)^{1/2}$ is the thermal velocity of the electrons. Thus it is evident that the forward characteristic is related to the concentration N_{po} of the *neutral* acceptor centers, whereas the thermally stimulated conductivity yields the concentration N_{no} of the *negatively charged* acceptor centers.

The lifetime of the electrons is calculated from Equation (3). For room temperature, using the values $\mu_n = 500$ cm²/Vsec [12], $\sigma = 2 \times 10^{-10}$ $(\Omega\text{cm})^{-1}$, $\varepsilon = 10$, one obtains $\tau_n/\tau_{p\Omega} = 10^{-4}$ and $\tau_n = 5 \times 10^{-7}$ sec.

According to the Ashley-Milnes model, the electron lifetime may also be inferred in a different way from the voltage V_Ω which characterizes the transition from ohmic to square law behavior of the forward characteristic. This voltage is reached, when the lifetime and the transit time of the electrons are comparable [14]:

$$V_\Omega = \frac{L^2}{\mu_n\, \tau_n}. \tag{6}$$

Extrapolating the square law portion of the forward characteristic yields the intersection with the ohmic portion at $V_\Omega \cong 1.5 \times 10^{-2}$ V, and together with $L = 2 \times 10^{-3}$ cm and $\mu_n = 500$ cm²/Vsec, Equation (6) yields $\tau_n = 5 \times 10^{-7}$ sec, which agrees with the first calculation.

Having determined the electron lifetime in two different ways, the concentration N_{po} of the neutral acceptor centers is obtained from Equation (5). Assuming $S_n = 10^{-15}$ cm² as a typical capture cross section of a neutral center [15] and setting $v = 10^7$ cm/sec, Equation (5) yields $N_{po} = 2 \times 10^{14}$ cm^{-3}.

The Ashley-Milnes model also provides an explanation for the strong rise in current at about 50 V (see Fig. 3). According to this model, the population of the recombination centers varies with the forward bias. The change ΔN_p in the concentration of the neutral centers may be positive or negative, depending on the ratio of the lifetime of the electrons and the dielectric relaxation time of the holes [14, 16]. For $\tau_n < \tau_{p\Omega}$ (in our case $\tau_n/\tau_{p\Omega} = 10^{-4}$) ΔN_p is negative and given by [14]:

$$\Delta N_p = N_p - N_{po} = -\frac{\tau_{p\Omega}}{\tau_n}\, n \tag{7}$$

where n is the electron concentration under forward bias V. We calculate this change at the onset of the strong increase of the forward current at about 50 V. Extrapolating the square law portion of the characteristic to 50 V, we assume that the corresponding current is carried only by electrons. Then their concentration is given by the mobility ($\mu_n = 500$ cm²/Vsec) and the conductivity at 50 V: $n = 9 \times 10^9$ cm^{-3}. Using the value

$\tau_n/\tau_{p\Omega} = 10^{-4}$, Equation (7) yields $\Delta N_p = 9 \times 10^{13}$ cm^{-3}. This result is in satisfying agreement with the space charge accumulated in the crystal under a forward bias of 50 V. The space charge Q_{sc} is given by the applied voltage V and the geometric capacitance C of the crystal, i.e. of the space-charge filled dielectric:

$$Q_{sc} = e\,N = \frac{C\,V}{A\,L} \tag{8}$$

with

$$\frac{C}{A} = \frac{2\,\varepsilon\,\varepsilon_0}{L}. \tag{9}$$

The quantity N is the concentration of the charged centers giving rise to the space charge. Using the dimensions of the epitaxial layer and assuming $\varepsilon = 10$, one obtains from Equations (8) and (9): $C/A = 10^{-9}$ Asec/Vcm^2 and N (50 V) $= 1.6 \times 10^{14}$ cm^{-3}.

Since the equilibrium concentration of the neutral centers and its decrease at 50 V have about the same values ($N_{po} \cong 2 \times 10^{14}$ cm^{-3} and $\Delta N_p \cong 1 \times 10^{14}$ cm^{-3}), the supply of neutral centers tends to become exhausted. Hence, the strong increase in current at about 50 V is attributed to the exhaustion of electron-capturing centers.

C. *Energy Location of the Acceptor Centers*

It has been postulated that the centers found from the thermally stimulated conductivity are identical to the acceptor centers of the Ashley-Milnes model. Therefore, their energy $E_t - E_v$ determined from the thermally stimulated conductivity has to be equal to the energy $E_a - E_v$ of the acceptor centers given by their population and the position of the equilibrium Fermi level.

Since it has been concluded that the acceptor centers are mostly occupied by electrons ($N_{no} > N_{po}$), their energy has to be located below the equilibrium Fermi level. For a partially compensated semiconductor containing N_d donors and N_a acceptors ($N_a > N_d$) the following relation holds between the energy E_a of the acceptor level, the equilibrium Fermi energy E_{Fo} and the impurity concentrations [17]:

$$E_a - E_v = E_{Fo} - E_v - k\,T \ln\left(\frac{2\,N_d}{N_a - N_d}\right). \tag{10}$$

Inserting the donor and acceptor concentrations $N_d = N_{no} = 2 \times 10^{15}$ cm^{-3} and $N_a = N_{no} + N_{po} = 2.2 \times 10^{15}$ cm^{-3}, and the value of the Fermi energy $E_{Fo} - E_v = 0.68$ eV, one obtains from Equation (10) for room temperature $E_a - E_v = 0.60$ eV. This energy is in excellent agreement with the energy of the hole trap $E_t - E_v = 0.61$ eV deduced from the thermally stimulated conductivity peak at 207 °K.

IV. Conclusions

Semi-insulating, iron-doped $GaAs_{0.5}P_{0.5}$ contains deep lying acceptor centers located 0.61 eV above the valence band and acting as hole traps. The total concentration of these centers is about 2×10^{15} cm^{-3}. It is shown that thermally stimulated conductivity measurements provide the concentration of the *ionized* centers ($N_{no} = 2 \times 10^{15}$ cm^{-3}), and space charge limited current measurements that of the *neutral* centers ($N_{po} = 2 \times 10^{14}$ cm^{-3}). The analysis of the forward current voltage charac-

teristic is based on a two carrier model by Ashley and Milnes, which is consistent with all experimental results.

V. Acknowledgments

The thermally stimulated conductivity measurements have been suggested by Drs. L. R. WEISBERG and R. WILLIAMS. The author wishes to thank them as well as Dr. J. J. TIETJEN for helpful and stimulating discussions. Thanks are also due to Dr. R. WILLIAMS for providing the sample used in this work, and to B. J. SEABURY for assistance in the measurements.

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Crystal Form and Crystal Structure

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(19. IV. 68)

Abstract. The observed geometry and frequency of occurrence of the forms of crystals of a given species (barite) are cast in the form of a weighted reciprocal lattice. Fourier transform yields crude electron density maps with some details of the structure. The proportionate specific surface energies of the forms derived from the observed distribution in geological time and space, show significant agreement with the calculated potential energies (structure factors) associated with appropriate reciprocal lattice points.

The relationship of the crystal form to a periodic internal structure was discussed quantitatively by BRAVAIS [1] who related the planes of cleavage and the planes of