

Compensation mechanisms in GaAs

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Semi-insulating GaAs materials, undoped or doped with concentration of chromium varying from 6×10^{15} to 4×10^{17} cm^{-3} , have been studied using both Hall effect measurements and optical absorption measurements. It is definitively concluded that compensation comes from the presence of the deep donor EL2 in undoped materials, and from both this deep donor and the deep acceptor related to chromium in Cr-doped materials. Sets of curves are given which allow the determination of $N_D - N_A$, the concentration of shallow donors and acceptors, knowing the Hall mobility and the Cr concentration in a given sample. Such curves can be a working tool for assessing any piece of semi-insulating GaAs in a routine way.

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I. INTRODUCTION

Studies dealing with the growth of semi-insulating GaAs have been conducted for about twenty years. At the beginning of the sixties, different methods were used by Ainslie *et al.*¹ and Woodall and Woods² to get GaAs materials with high resistivity, namely, the Bridgman technique with oxygen doping^{1,2} and the floating-zone technique.³ But the electrical properties of the materials were not reproducible. Cronin and Haisty⁴ have shown that Czochralski-grown material, doped with chromium, could be made semi-insulating in a repetitive way. Further studies have concentrated on the means allowing purification of the material and reduction of the residual doping of the undoped ingots. As far as the Bridgman growth is concerned, the effect of oxygen doping has particularly been studied; Woods and Ainslie have shown that it allows significant reduction of the residual doping and the obtaining of a purer material with better mobilities.⁵ The method of obtaining, in this way, the most homogeneous material seems to have been perfected by Shimoda.⁶ Furthermore, the presence of the boric-oxide encapsulant in the Czochralski growth has led to high-resistivity materials without intentional doping.⁷ This technique, called LEC, has been investigated by numerous authors who have studied the contamination due to different crucible materials like silica, alumina, or pyrolytic boron nitride,^{8,9} and who have proved that the undoped material could be highly resistive.

The characterization of these materials has mainly been done by Hall effect measurements. In the case of nonintentionally doped and high-resistive materials, the Hall data have been interpreted assuming the presence of a deep level,^{5,10,11} having an enthalpy of 0.75 eV below the bottom of the conduction band. The characterization of semi-insulating materials doped with different amounts of chromium has been resumed more recently by Zucca,¹² Lindquist,¹³ and Look.¹⁴ No definite conclusion on the compensation mechanisms can be drawn, since different models have been proposed to explain the Hall effect data. In the first case,¹² the model uses a Cr acceptor level and a deep donor level located

above the Cr level in the band gap. The second model still uses a Cr acceptor level and a deep donor level, but the hypothesis is made that the donor level is located below the Cr level in the band gap. In the third case,¹⁴ all the Hall results have been interpreted using only a deep acceptor related to chromium. Furthermore, Lindquist and Look have made attempts to correlate the impurity concentration measured by chemical analysis with the concentration of the shallow and deep levels needed to fit the Hall effect curves. At this time, we should note that in both studies the concentration of the deep donor was assumed to be equal to that of oxygen.

In this paper, we are going to show how the Hall data depend on the relative concentration of two deep levels (N_{DD} for the deep donor and N_{AA} for the Cr acceptor level), and of the shallow donors N_D and acceptors N_A . More especially, it will be shown that the combination of the optical absorption measurements, which provide N_{AA} ,¹⁵ with the Hall effect measurements, allows a clear assessment of a given semi-insulating material, i.e., the evaluation of the values of N_{DD} , N_D , and N_A with a reasonable accuracy. Such a characterization, involving both Hall effect and optical absorption measurements, can be done in a routine way and does not need any computer fitting of the full Hall curves.

II. STATE OF THE ART CONCERNING THE DEEP LEVELS IN SEMI-INSULATING GaAs

Owing to a technique used for the spectroscopy of deep levels in insulating materials, called OTCS (Optical Transient Current Spectroscopy),¹⁶ it has been shown that two levels are usually present in semi-insulating GaAs in the largest concentration: an electron trap, labeled EL2 in the largest paper,¹⁷ which is a deep donor level, and a hole trap, which is a deep acceptor related to chromium. These two levels have already been studied in detail in our laboratory. The aim of the characterization of these two levels has been to obtain their Fermi function f as a function of temperature, and more especially at high temperature where Hall measurements are carried out. The function f is given by the well-known expression¹⁸

$$f = \left[1 + \frac{g_0}{g_1} \exp \left(\frac{(E_C - E_F) - (E_C - E_T)}{kT} \right) \right]^{-1}, \quad (1)$$

where

$$E_C - E_T = \Delta H - T\Delta S \quad (2)$$

is the free energy of ionization of the level, ΔH is its enthalpy, and ΔS is its entropy. g_0 is the degeneracy of the level not occupied by an electron, and g_1 is the degeneracy of the level occupied by the electron. It has been shown how the detailed electrical characterization¹⁹ of a level allows the determination, as a function of temperature, of the following function:

$$E' = E_C - E_T - kT \ln(g_0/g_1), \quad (3)$$

$$E' = \Delta H - T\Delta S - kT \ln(g_0/g_1). \quad (4)$$

Knowing this function, one can deduce without any ambiguity or assumption the corresponding Fermi function f .

A. Deep donor EL2

Let us first consider the deep donor EL2. Measurements of the electron capture cross section²⁰ and of the electron emission rate¹⁷ have provided the function E' , also obtained by more direct measurements²¹:

$$E'(\text{EL2}) = 0.759 - \alpha T - kT \ln(g_0/g_1) \quad \text{eV}, \quad (5)$$

$$E'(\text{EL2}) = 0.759 - [\alpha + k \ln(g_0/g_1)]T \quad \text{eV}, \quad (6)$$

with

$$[\alpha + k \ln(g_0/g_1)] = 2.37 \times 10^{-4} \text{ eV} \times k^{-1}. \quad (7)$$

Equation (5) is a linear approximation of Eq. (4), shown to be valid at high temperature, i.e., at least between 300 and 450 °K.²¹

Furthermore, Mircea and Mitonneau proved that this deep level EL2 is a donor.²² There was still another important question about the nature of this level, frequently assumed to be related to oxygen in the literature. A recent study²³ has given a clear and definite conclusion: EL2 is not related, directly or indirectly, to the presence of oxygen. Consequently, previously published works in which the concentration of the deep donor was taken equal to the concentration of oxygen are doubtful.

If the nature of EL2 remains unknown, some information is available concerning its concentration N_{DD} . In epitaxial layers, it ranges generally between 10^{14} and 10^{15} cm^{-3} .²²

In n -type bulk GaAs, it is much larger, generally of the order of a few 10^{16} cm^{-3} in Bridgman²³ or Czochralski²⁴ materials. Furthermore, in several semi-insulating bulk materials studied by the OTCS technique,¹⁶ the concentration [EL2] was measured to be larger than a few 10^{16} cm^{-3} .

B. Deep chromium acceptor

The following will review the previously published results concerning the incorporation and the electrical properties of Cr in GaAs. The assessment of a very large number of various GaAs materials, semi-insulating¹⁶ or conductive,¹⁹ has shown that chromium introduces a unique deep acceptor level.

It has been established that most of the Cr atoms, if not

all of them, incorporated in GaAs are active and correspond to this deep acceptor level. This study¹⁹ has been done, using DLTS, in a material with a Cr concentration around 10^{16} cm^{-3} . In the case of larger concentration, from 10^{16} up to $2 \times 10^{17} \text{ cm}^{-3}$, it has been observed that the absorption coefficient in the infrared increases linearly with the Cr content,¹⁵ which confirms the validity of the above conclusion: most of the Cr atoms are active in semi-insulating GaAs up to concentrations of the order of several 10^{17} cm^{-3} . This justifies the fact that in the present work the concentration of the deep acceptor will be taken equal to the concentration of Cr deduced from optical absorption.

The peculiar electrical behavior of the Cr level has already been studied in detail.¹⁹ Due to its depth and to the properties of its electron capture cross section, this level can be detected as an electron trap or a hole trap, according to its refilling state. This is an exceptional behavior in GaAs. From the hole emission and capture rate data, we have obtained a precise evaluation of the function E' relative to the top of the valence band in the form of the following expression which is valid at any temperature¹⁹:

$$E'(\text{Cr}) = \Delta H(T=0) - \frac{\alpha_p T^2}{T+204} + kT \ln(g_0/g_1). \quad (8)$$

The measurements did not yield each of the parameters $\Delta H(0)$, α_p , and g_0/g_1 separately, but sets of these parameters can be found leading to nearly identical values of E' for $T > 50$ °K. The following set can be chosen arbitrarily to give the right values of E' :

$$E'(\text{Cr}) = 0.81 - \frac{(3 \times 10^{-4})T^2}{T+204} + kT \ln 0.93 \quad \text{eV}, \quad (9)$$

where E' is given relative to the valence band. The Fermi function f , for the Cr level, can be calculated in this way, according to Eqs. (1) and (3):

$$f(\text{Cr}) = \left[1 + \exp \left(\frac{+(E_C - E_F) - E_G + E'(\text{Cr})}{kT} \right) \right]^{-1}, \quad (10)$$

where E' is given by Eq. (9) and E_G is the band gap given by²⁵

$$E_G = 1.519 - \frac{(5.4 \times 10^{-4})T^2}{T+204} \quad \text{eV}. \quad (11)$$

III. EXPERIMENTAL TECHNIQUES

Most of the GaAs crystals discussed here have been grown using the horizontal Bridgman technique. Compounding and growth are performed in the same sealed ampoule using a silica boat. Crystal weight is about 1000 g and the seed is (111) oriented. Chromium doping is performed by adding metallic chromium to the melt; oxygen doping is obtained using Ga_2O_3 .

Wafers of other semi-insulating ingots were purchased from several suppliers. Growth technique is either Bridgman or Czochralski (liquid encapsulated) and this is mentioned in the following, according to the supplier comments. A few LEC samples pulled by Metals Research and at the Naval Research Laboratory have also been tested.

In accordance with previous work,^{5,9} it will be assumed

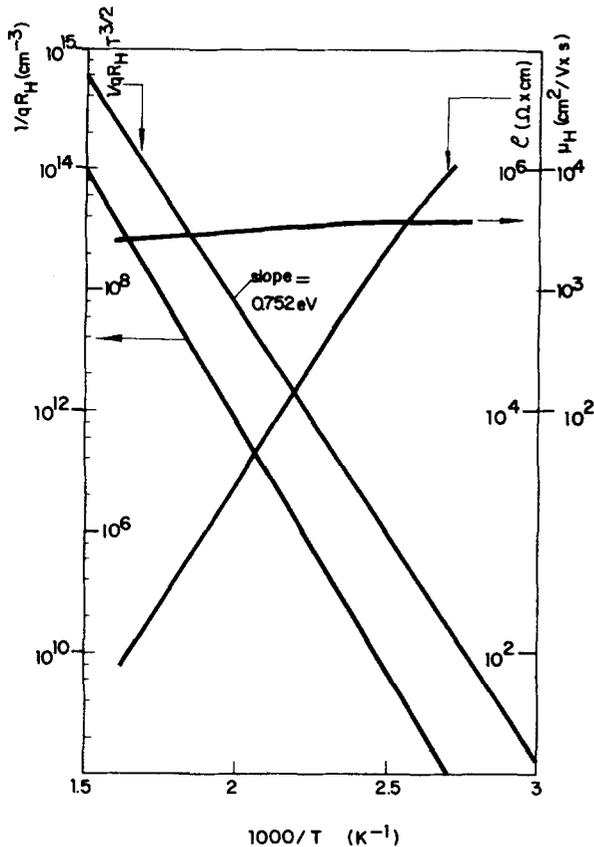


FIG. 1. Typical curves of μ_H , $1/qR_H$, and resistivity recorded as a function of the reciprocal value of temperature on semi-insulating GaAs, from Hall effect measurements.

that an oxygen overpressure in Bridgman growth reduces the silicon contamination and that the boric oxide cap used in LEC also minimizes pollution when silica boats (or crucibles) are used.

Hall data over the temperature range 700–300 °K have been obtained using the standard Van der Pauw technique.²⁶

Results are plotted as $1/qR_H$, $(R_H T^{3/2})^{-1}$, and mobility against $1/T$. Typical results are shown in Fig. 1.

Experimental data used in the following are taken at 400 °K. This temperature is high enough to avoid any surface-related error in the Hall measurement, but low enough to allow neglecting n and p (free carriers) with respect to the concentration of ionized levels.

IV. RESULTS

A. High resistivity GaAs not doped with chromium

1. Results

The results of Hall effect measurements on a few semi-insulating undoped GaAs ingots are reported in Table I. Each of the measurements presented in this table have in fact been obtained several times on several materials, and Table I is a selection from a large number of materials of similar properties. The values at $T = 400$ °K of the apparent Hall mobility μ_H and of the inverse of the Hall constant R_H , which is proportional to the free carrier concentration on low resistivity materials, are reported, together with the value of the slope S of the Arrhenius plot of $(qR_H T^{3/2})^{-1}$ measured between 350 and 650 °K.

In the following, we will simply call μ_H the Hall mobility (instead of the apparent Hall mobility), μ_H being in any cases equal to $R_H \sigma$, where σ is the conductivity. Three kinds of materials are found: (i) the materials A1–A3 in which the slope is equal to 0.76 eV and the mobility μ_H large; (ii) the materials A4–A9 in which the slope S is in the range 0.35–0.6 eV and the mobility is lower than in the previous case; and (iii) the materials A9 and A10 in which the slope S is close to 0.76 eV and the mobility is low.

The electrical properties of these materials can be explained by the presence of the deep donor EL2.

Before all, it may be remembered that in highly resistive material, the Hall constant and the Hall mobility are given by the expression¹²

TABLE I. Results on Hall effect measurements carried out on semi-insulating GaAs not doped with Cr. N_V is deduced from μ_H , using Fig. 2.

Material	Hall effect data				$E_C - E_F$ at 400 °K (eV)
	$(qR_H)^{-1}$ at 400 °K (cm ⁻³)	μ_H at 400 °K (cm ² /V s)	Slope of $\ln(R_H T^{3/2})^{-1} = f(1/T) N_V$ (eV)	N_V (cm ⁻³)	
A1 Bridgman	1.1×10^{11}	4500	0.757	3×10^{16}	0.539
A2 Bridgman	1.7×10^{10}	4500	0.729	3×10^{16}	0.604
A3 Bridgman	1.3×10^{11}	5500	0.750	4×10^{15}	0.533
			slope of $\ln(R_H T^{3/4})^{-1} = f(1/T)$		
A4 Bridgman	2.5×10^{13}	4300	0.350	5×10^{16}	0.352
A5 Bridgman	1.5×10^{13}	4300	0.422	5×10^{16}	0.370
A6 Bridgman	2.8×10^{13}	2500	0.392	5×10^{17}	0.348
A7 LEC	1.6×10^{11}	2800	0.600	4×10^{17}	0.526
A8 Bridgman	8×10^{13}	1700	0.164	...	0.312
			slope of $\ln(R_H T^{3/2})^{-1} = f(1/T)$		
A9 LEC	4×10^9	1850	0.728		0.653
A1 LEC	1.1×10^{10}	2600	0.762		0.619

$$\frac{1}{qR_H} = \frac{1}{r_H} \frac{[p + n(\mu_n/\mu_p)]^2}{p - n(\mu_n/\mu_p)^2} \quad (12)$$

and

$$\mu_H = r_H \mu_n \left(\frac{n - p(\mu_p/\mu_n)^2}{n + p(\mu_p/\mu_n)} \right), \quad (13)$$

where μ_n and μ_p are the electron and hole mobilities, their ratio being taken¹⁰ equal to 15 in our calculation at 400 °K. It can be noted that, at this temperature, the depth of the Fermi level below the conduction band, for which n is equal to p , is 0.637 eV. All the materials of Table I appear n type ($R_H < 0$) in Hall measurements. The depth of the Fermi level has been calculated for each of them, assuming that $(qR_H)^{-1} = n \gg p$. In the case of materials A1–A8, the value obtained is distinctly lower than 0.637 eV; thus the assumption is valid and $\mu_H = r_H \mu_n$. This is not the case for materials A9 and A10, but this case will be studied later on. Also, it should be noted that in view of the rather large value of μ_n/μ_p , a p -type material may well exhibit a negative value of R_H .

The equation of neutrality of charges is given by the following expression, taking into account the shallow donor N_D and acceptor N_A , as well as the deep donor N_{DD} = [EL2]:

$$n = p + N_D^i + N_{DD}^i - N_A^i, \quad (14)$$

where the superscript corresponds to "ionized." In view of the depth of the Fermi level, we have $N_D^i = N_D$ and $N_A^i = N_A$. Equation (14) simplifies to

$$n = N_{DD} [1 - f(\text{EL2})] - (N_A - N_D), \quad (15)$$

where $f(\text{EL2})$ is given by Eq. (1). Using $n = N_C \exp[-(E_C - E_F)/kT]$, we obtain

$$n = \frac{N_{DD} N_C \exp[-(E_C - E_T)/kT]}{n(g_1/g_0) + N_C \exp[-(E_C - E_T)/kT]} - (N_A - N_D), \quad (16)$$

where $(E_C - E_T)$ is the free energy for ionization of the deep donor.

Simplified expressions⁵ can be obtained for n in two cases:

if $n \ll (N_A - N_D)$,

$$n = [N_{DD}/(N_A - N_D) - 1] N_C \exp[-E'(\text{EL2})/kT], \quad (17)$$

or, using Eq. (6),

$$n = [N_{DD}/(N_A - N_D) - 1] N_C (g_0/g_1) \times \exp(\alpha/k) \exp(-0.759 \text{ eV}/kT), \quad (18)$$

if $(N_A - N_D) \ll n$, which is a very drastic condition, and if $n \gg (g_0/g_1) N_C \exp[-(E_C - E_T)/kT]$ (a condition which is often fulfilled, since the last term is equal to 3×10^9 at 400 °K), one gets the other expression:

$$n = [N_C N_{DD} (g_0/g_1)]^{1/2} \times \exp(\alpha/2k) \exp(-0.759 \text{ eV}/2kT). \quad (19)$$

In this case, everything happens as if the deep level EL2 was alone in the material. This is coherent with the previous condition which corresponds to a completely negligible value of $(N_A - N_D)$.

V. DISCUSSION

A. Materials with steep slopes of $R_H(T)$ and high mobilities

This is the case of materials A1–A3 in Table I. As noted above, in these materials the Fermi level is not too deep, since $(qR_H)^{-1} \gtrsim 10^{11} \text{ cm}^{-3}$ at 400 °K and thus $n \gg p$. The relations $(qR_H)^{-1} = n$ and $\mu_H = r_H \mu_n$ can be taken. The experimental slope S of the Arrhenius plot of $nT^{-3/2}$ is equal to 0.75–0.76 eV. This is quite in agreement with Eq. (18), which corresponds to the presence of the deep donor EL2. Since we know $E'(\text{EL2})$, we can deduce the ratio $N_{DD}/(N_A - N_D)$, which amounts to 30–40 in the investigated A1–A3 materials.

Taking N_{DD} = [EL2] equal to a few 10^{16} cm^{-3} , and using the condition of validity of Eq. (17), it can reasonably be assumed that in this kind of material, the value of $(N_A - N_D)$ lies in the following range:

$$10^{11} \ll (N_A - N_D) \leq 10^{15} \text{ cm}^{-3}.$$

B. Materials with intermediate slopes of $R_H(T)$

This is the case corresponding to materials A3–A8 in Table I. Their resistivity is still lower than the resistivity of materials A1–A3 and $(qR_H)^{-1} = n$, generally of the order of 10^{13} cm^{-3} at 400 °K. The experimental values of the slopes of the Arrhenius plot of $nT^{-3/4}$ are scattered around 0.4 eV, but not very far from 0.38 eV which is the value predicted by Eq. (19). The corresponding approximation is very drastic, since $N_A - N_D$ must be lower than n , which is equal to 10^{13} cm^{-3} at 400 °K in these materials. Such very low values of $N_A - N_D$ are amazing and probably rather fortuitous. Large fluctuations of $N_A - N_D$ are thus easily conceivable, leading to important variations of the slope of $n(T)$, as it is observed in materials A4–A6. These fluctuations exist in the same ingot: sample A4 was cut from the seed side on an ingot [and $(N_A - N_D) < 10^{13} \text{ cm}^{-3}$, in this case], whereas sample A5 was cut from the tail side of the same ingot [$(N_A - N_D) \simeq 10^{15} \text{ cm}^{-3}$, as deduced above]. These fluctuations have even been observed to exist in a same slice between samples cut very close to one another.

The fluctuation of the slope of $n(T)$ in different samples cut in the same material, around 0.4 eV, is very compatible with the present analysis based on EL2, as the main deep level. Another analysis based on the presence of other deep levels different in each different material is possible, but may be less coherent with the low value of μ_H . There are actually some deep levels which could be responsible for the slopes observed, for instance EL6 for sample A4, EL5 for samples A5 and A6, EL3 for sample A7, and EL11 for sample A8, since the apparent activation energy of these levels was measured¹⁷ to be 0.35, 0.42, 0.575, and 0.17, respectively. But only EL2 has been observed in the large concentration and in a reproducible way in undoped GaAs, using the spectroscopic DLTS and OTCS techniques.^{16,17}

According to Eq. (19), it is possible to get an estimation of N_{DD} = [EL2],

$$[\text{EL2}] = (n^2/N_C) \exp[E'(\text{EL2})/kT]. \quad (20)$$

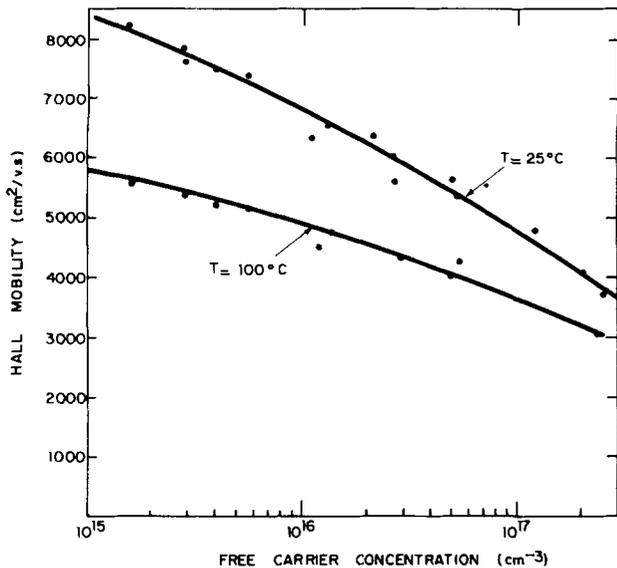


FIG. 2. Plots of the Hall mobility as a function of the electron free carrier concentrations in very high purity vapor phase epitaxial layers. The measurements have been done on the same samples at 25 and 100 °C.

Using the value of $n(400\text{ °K})$ given in Table I and Eq. (6), one obtains

$$2 \times 10^{16} < [\text{EL2}] < 2 \times 10^{17} \text{ cm}^{-3}$$

for material A6; the uncertainty coming from the uncertainty of the value of $[\alpha + k \ln(g_0/g_1)]$ in Eq. (7)²¹ and from the fact that the slope S is not exactly equal to $\frac{1}{2}(0.759) \text{ eV}$. The above values are only indicative, but they do confirm the order of magnitude of the concentration [EL2].

C. Interpretation of Hall mobilities in the two previous cases

As discussed above, in materials A1–A8, n is much larger than p and the Hall mobility is equal to $r_H \mu_n$. Figure 2 gives the experimental value of the electron mobility measured by the Hall effect at 20 and at 100 °C in epitaxial layers (VPE) doped from 10^{15} to $3 \times 10^{17} \text{ cm}^{-3}$. Making the sim-

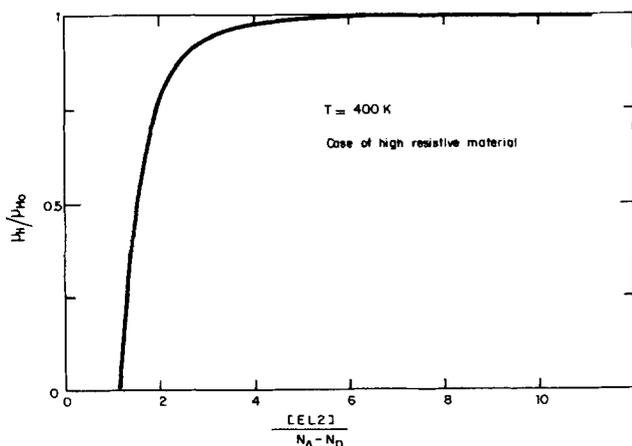


FIG. 3. Variation of μ_H/μ_n as a function of the ratio of the deep donor EL2 over $(N_A - N_D)$, deduced from the electrical properties of the deep donor EL2.

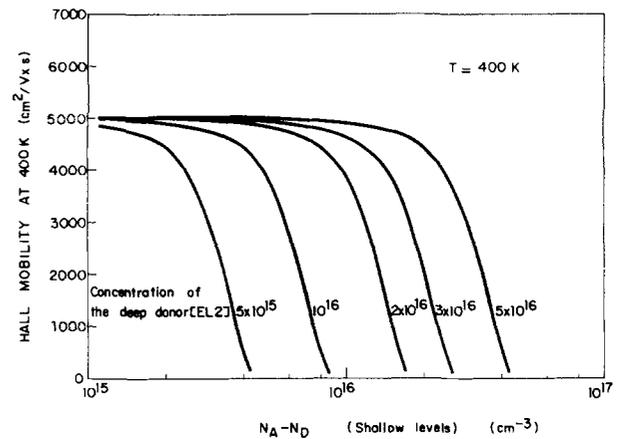


FIG. 4. Variation of the Hall mobility μ_H as a function of $(N_A - N_D)$ (the concentration of shallow acceptors and donors), for different values of concentration of the deep donor EL2. The electron mobility μ_n is taken equal to $5000 \text{ cm}^2/\text{V s}$.

plest hypothesis that these layers are not compensated and that n is equal to the total concentration of ionized impurities, one can deduce from Fig. 2 the value of the concentration of ionized levels corresponding to each value of mobility. This concentration is very close to $(N_A + N_D)$, since the deep donor EL2 is almost not ionized in the present cases. Such values of $(N_A + N_D) = N_i'$ are reported in Table I, deduced by this way in each case.

As for the materials A1–A3, the values obtained for $N_A + N_D$ are equal to 4×10^{15} and 3×10^{16} . This is plausible and coherent with the values of $N_A - N_D$ estimated above to be about 10^{15} cm^{-3} . Oppositely in the case of materials A4–A8, it was established above that $N_A - N_D$ should be lower than 10^{13} cm^{-3} , while the present analysis gives values of $N_A + N_D$ ranging between 5×10^{16} and $4 \times 10^{17} \text{ cm}^{-3}$. It seems very unlikely that the ratio $(N_A - N_D)/(N_A + N_D)$ could be equal to 10^{-4} . This suggests that the ionized impurities scattering is not the dominant mechanism in this last case. More probably, the low mobilities observed could be due to microscopic inhomogeneities in the material. The influence of random inhomogeneities has been studied, by Herring,²⁷ and the general conclusion is that the measured values of the mobility and of the conductivity are lower than the mean values. Most of the studies dealing with other types of inhomogeneities and reviewed by Blood and Orton²⁸ lead to similar conclusions. These results compare well with the observations in the materials investigated, in which large fluctuations of $N_A - N_D$ are expected, leading to large fluctuations of the conductivity of the material on a microscopic scale.

D. Materials with steep slopes of R_H and low mobilities

Consider now the case of a very-high-resistivity material, for which typically $(qR_H)^{-1} < 10^{11} \text{ cm}^{-3}$ at 400 °K, and the slope of the Arrhenius plot of $(qR_H T^{3/2})^{-1}$ is large, i.e., 0.75 eV. This kind of material is well illustrated by the samples A9 and A10 in Table I. n and p , then, have similar values, of the order of 10^{10} cm^{-3} at 400 °K. The Hall mobility is an apparent reduced mobility, according to Eq. (13).

TABLE II. Results obtained by Hall effect measurements and optical absorption measurements on semi-insulating GaAs heavily doped with Cr, and with different concentration of silicon.

Material	Optical absorption data Concentration of chromium (cm ⁻³)	Hall effect data			
		(qR _H) ⁻¹ at 400 °K (cm ⁻³)	μ _H at 400 °K (cm ² /V s)	Type	Concentration of silicon (cm ⁻³)
B1 Bridgman	1.4 × 10 ¹⁷	8.5 × 10 ⁹	1950	n	≈ 3 × 10 ¹⁶
B2 Bridgman	(8-10) × 10 ¹⁶	4.5 × 10 ⁹	3200	n	≈ 5 × 10 ¹⁶
B3 Bridgman	3 × 10 ¹⁷	1.7 × 10 ¹⁰	820	n	a few 10 ¹⁶
B4 Bridgman	(3-4) × 10 ¹⁷	2.8 × 10 ¹⁰	360	n	≈ 5 × 10 ¹⁶
B5 LEC	3 × 10 ¹⁷	ρ = 2 × 10 ⁵ Ω cm	100	p	0

Furthermore, the equation of neutrality, Eq. (5), simplifies to the following expression at 400 °K:

$$N_{DD}^i = N_A - N_D, \quad (21)$$

from which we can deduce the Fermi level, i.e.,

$$E_C - E_F = E_C - E_T - kT \ln \frac{g_0}{g_1} - kT \ln \left(\frac{N_{DD}}{N_A - N_D} - 1 \right) \quad (22)$$

$$E_C - E_F = E'(EL2) - kT \ln \left(\frac{N_{DD}}{N_A - N_D} - 1 \right), \quad (23)$$

where E'(EL2) is given by Eq. (6).

Knowing the Fermi level and μ_n/μ_p = 15 (see above), one can calculate n and p, and thus the ratio μ_H/μ_n, where μ_H = r_Hμ_n is the true electron mobility which would be obtained if n were much larger than p. The variation of μ_H/μ_n has been calculated as a function of the compensation ration [EL2]/(N_A - N_D), as shown on Fig. 3. It is clear that the Hall mobility is reduced if this ratio is lower than 4. In the case of materials A9 and A10, the low mobility, around 2000 cm²/V s, indicates that the compensation ratio is low, of the order of 2. Assuming that [EL2] is equal to a

few 10¹⁶ cm⁻³, this leads to a value of N_A - N_D of the order of 10¹⁶ cm⁻³. This high value is well explained¹⁰ by the fact that the material A9 was doped with Zn, and the material A10 is expected to be polluted by acceptors.

Using the same calculations as for Fig. 3, we have plotted the Hall mobility μ_H as a function of N_A - N_D, for different values [EL2], taking the electron mobility to be equal to 5000 cm²/V s, (see Fig. 4). This set of curves may be more clear and convenient in routine analysis.

In conclusion, one can note that in these high-resistive materials not doped with Cr, N_A is larger than N_D, and N_A - N_D is generally low (around 10¹⁵ cm⁻³) and sometimes very low (< 10¹³ cm⁻³). The only case where N_A - N_D is larger (around 10¹⁶ cm⁻³) corresponds to an increase of N_A. This suggest that (i) the residual concentration of N_A in the investigated materials, especially Bridgman materials, is about a few 10¹⁵ cm⁻³ and (ii) the concentration of N_D, which must be lower than N_A, is also very low, lower or equal to 10¹⁵ cm⁻³. At this point, it is worth noting that the Bridgman material A1 was doped with oxygen, while the other Bridgman materials A2-A6 were not intentionally doped with oxygen.

E. Chromium-doped GaAs ingots

A different type of semi-insulating GaAs will be now be reported on. All the materials presented in this section have been selected using optical absorption measurements,¹⁵ which allowed the determination of the Cr content in each case and the choice of homogeneous materials exclusively.

1. GaAs heavily doped with Cr ([Cr] > 10¹⁷ cm⁻³)

The list of these samples, together with their Cr concentration, are given in Table II. All the reported materials present a high resistivity. The value of (qR_H)⁻¹ is quite low, in all cases lower than 5 × 10¹⁰ cm⁻³. Two types of materials can be distinguished: (i) the materials which appear n type (R_H ≤ 0) and (ii) those which appear p type (R_H > 0). It will be shown that the electrical properties of the Cr level, established in great detail, allow taking into account both the mobility and the sign of the Hall constant R_H.

Let us now write the equation of neutrality of charges, taking into account the shallow donors N_D and acceptors N_A

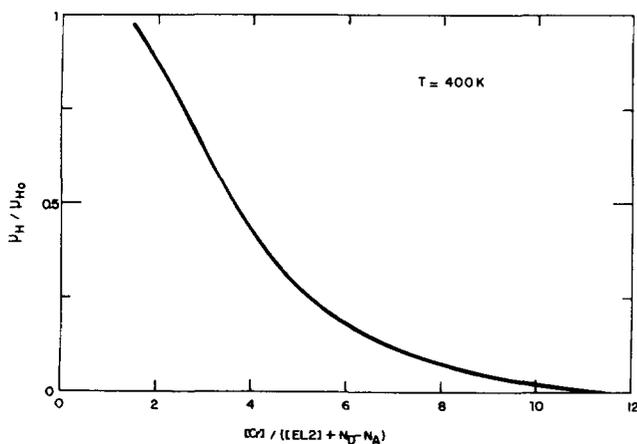


FIG. 5. Expected variation of the ratio μ_H/μ_n as a function of the ratio of the Cr concentration over the concentration of the deep donor EL2 plus N_D - N_A.

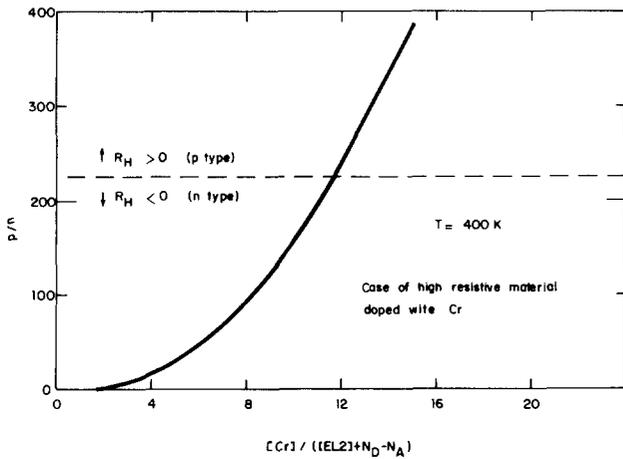


FIG. 6. Expected variation of the ratio p/n as a function of the ratio of the Cr concentration over the sum of the concentration of the deep donor EL2 and $N_D - N_A$. This figure should allow prediction when a semi-insulating GaAs material will appear n or p type in Hall measurements.

and the deep donor $N_{DD} = [EL2]$ and the deep acceptor $N_{AA} = [Cr]$:

$$n = p + N_D^i + [EL2]^i - N_A^i - [Cr]^i. \quad (24)$$

In the same way as above, n and p are negligible at 400 °K, in view of the very high resistivity of the material, and $N_A^i = N_A$, $N_D^i = N_D$. Furthermore, the concentration of the deep acceptor Cr, larger than 10^{17} cm^{-3} , is much larger than EL2, close to 10^{16} cm^{-3} . One can thus simplify, using $[EL2]^i = [EL2]$. This will be justified later on. Equation (24) reduces to

$$[Cr]f(\text{Cr}) = N_D + [EL2] - N_A, \quad (25)$$

leading to

$$E_F - E_V = E_T - E_V + kT \ln \frac{g_0}{g_1} - kT \ln \left(\frac{[Cr]}{[EL2] + N_D - N_A} \right) \quad (26)$$

$$E_F - E_V = E'(\text{Cr}) - kT \ln \left(\frac{[Cr]}{[EL2] + N_D - N_A} \right), \quad (27)$$

where $E'(\text{Cr})$ is given by Eq. (9). One can now calculate the Fermi level and thus n and p . As in the previous paragraph, the ratio of the Hall mobility μ_H to the true value of the electron mobility μ_{H_0} can be computed as a function of the compensation ratio $[Cr]/([EL2] + N_D - N_A)$. The curve is given in Fig. 5.

On the other hand, the Hall constant is given by Eq. (12). According to this equation, R_H becomes positive, and the material appears p type, when the ratio p/n is larger than $(\mu_n/\mu_p)^2$, assumed to be equal to 225 at 400 °K.¹⁰ It is thus useful to plot also the ratio p/n calculated as a function of the same compensation ratio. The curve is given in Fig. 6. It can be emphasized that no hypothesis, except μ_n/μ_p (400 °K) = 15, has been used to compute the results of Figs. 5 and 6, and that they are the results of detailed experiments on the corresponding deep levels. These figures can be used to get a

precise idea of the compensation ratio in any case, providing that the material is highly resistive $[(qR_H)^{-1} \leq 5 \times 10^{10} \text{ cm}^{-3}]$, at 400 °K and the Cr concentration is larger than 10^{17} cm^{-3} .

Shockley's diagram²⁹ is a good way to visualize the compensation mechanisms. In this diagram, drawn in Fig. 7, the concentration of the ionized levels is plotted as a function of the Fermi level; the intersection of the acceptors curve with the donors curve gives the graphical solution of the equation of neutrality (24). In Fig. 7, three cases are represented corresponding to three different values of the compensation ratio.

(1) *Materials with $R_H < 0$ (n type)*. Two kinds of materials can be crudely distinguished:

(i) the materials with a rather high mobility, as the samples B1 and B2 in Table III ($\mu_H = 1950$ and $3200 \text{ cm}^2/\text{V s}$). In these materials, the Cr concentration is near 10^{17} cm^{-3} . According to Fig. 2, the electron mobility should be around $4000 \text{ cm}^2/\text{V s}$ for a total number of ionized levels a bit lower. The ratio μ_H/μ_{H_0} is thus about 0.4 to 0.5 for material B1 and 0.8 for material B2. Using Fig. 5 and the accurate concentration of Cr reported in Table III, we obtain

$$\begin{aligned} [EL2] + N_D - N_A &= (3-4) \times 10^{16}, \text{ in material B1} \\ &= (4-5) \times 10^{16}, \text{ in material B2.} \end{aligned}$$

These values confirm that the concentration of the deep donor is of the order of some 10^{16} cm^{-3} . The concentration of silicon, responsible for N_D , determined by spark source mass spectroscopy was found³⁰ to be $2 \times 10^{16} \text{ cm}^{-3}$ in material B1, slightly doped with Si. The material B2 was also

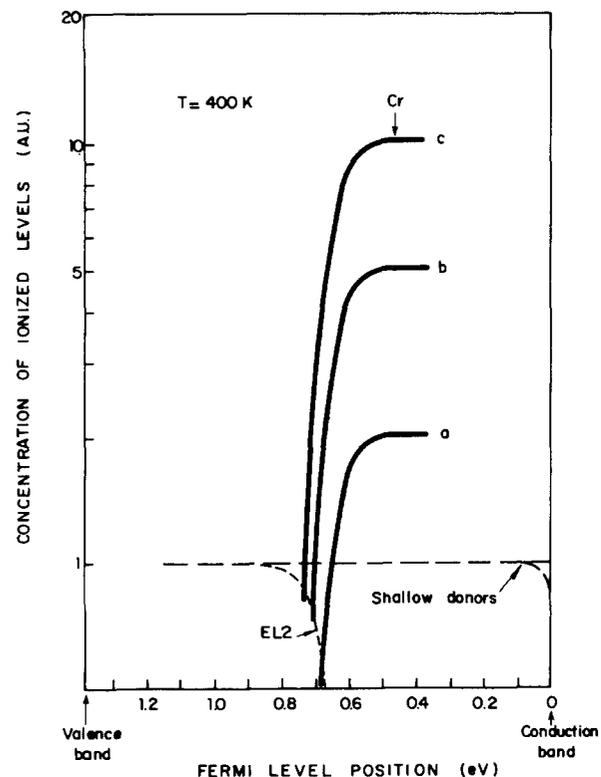


FIG. 7. Shockley diagram corresponding to three different values of the compensation ratio.

TABLE III. Results from Hall effect measurement and concentration of chromium in semi-insulating GaAs slightly doped with chromium.

Material	Concentration of chromium (cm ⁻³)	Hall effect data		
		(qR_H) ⁻¹ at 400 °K (cm ⁻³)	μ_H at 400 °K	Slope of $\ln(R_H T^{3/2})^{-1}$
C1 Bridgman	6 × 10 ¹⁵	1.2 × 10 ¹⁰	2800	0.771
C2 Bridgman	6 × 10 ¹⁵	4.6 × 10 ¹⁰	3200	0.679

doped with silicon and its concentration was expected to be around 5 × 10¹⁶ cm⁻³. As a matter of fact, another material grown in exactly the same conditions as B2, but without chromium doping had a free carrier concentration $N_D - N_A$ equal to (4–6) × 10¹⁶ cm⁻³.

From Fig. 6, the ratio p/n corresponding to a compensation ratio of 3–4 is 10, and R_H is negative. This is case (a), in the Shockley diagram of Fig. 7.

(ii) The materials with a low Hall mobility, as material B3 and B4, for which $\mu_H < 1000$ cm²/V s. In both materials, the Cr concentration is as large as 3 × 10¹⁷ cm⁻³. In fact, as shown in the Shockley diagram, only a small fraction of the Cr level is ionized and the electron mobility can still be assumed to be around 4000 cm²/V s. The ratio μ_H/μ_{H_0} is thus about 0.2 and from Fig. 5, the compensation ratio is

$$R_C = \frac{[Cr]}{[EL2] + N_D - N_A} = 6.$$

Using the Cr concentrations given in Table II, we get for both materials,

$$[EL2] + N_D - N_A \simeq (3-4) \times 10^{16} \text{ cm}^{-3},$$

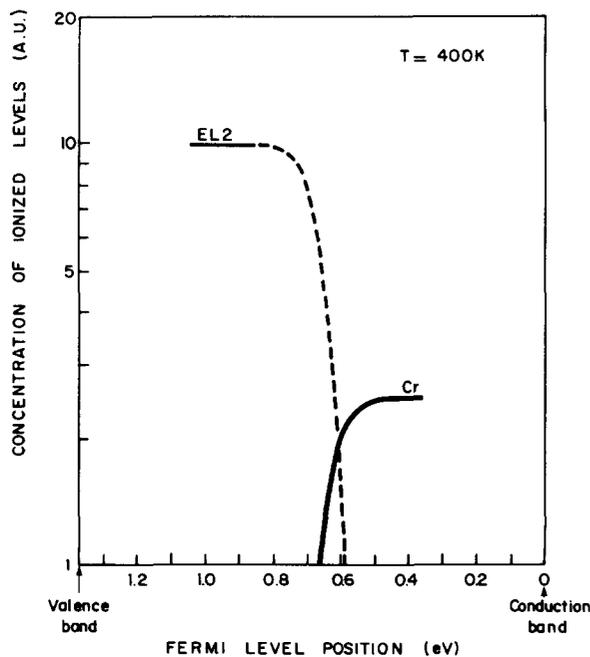


FIG. 8. Shockley diagram corresponding to a semi-insulating material with the deep donor (EL2) and acceptor (Cr), the shallow levels being negligible.

which leads to the same conclusion on [EL2] and N_D as for material B1, since B3 and B4 were also slightly doped with silicon.

It can be checked on Fig. 6 that p/n is equal to 100 for $R_C = 6$, which means that R_H is still negative. This corresponds to case (b) in Fig. 7.

(2) *Material with $R_H > 0$ (p type)*. This is the case of material B5 in Table II, which presents the same Cr concentration as materials B3 and B4. Since $R_H > 0$, one can conclude from Fig. 6 that

$$R_C = \frac{[Cr]}{[EL2] + N_D - N_A} \geq 11.5,$$

which leads to

$$[EL2] + N_D - N_A \leq 2.5 \times 10^{16} \text{ cm}^{-3}.$$

It is reasonable to think that this value, as compared to previous material B3, corresponds to the decrease of shallow donors N_D . As a matter of fact, the material B5 has been grown by the LEC technique and a large reduction of silicon is expected. It is very likely that the compensation of the material is insured by the presence of both deep levels, the acceptor Cr and the donor EL2 with a concentration near 2 × 10¹⁶ cm⁻³. Such a situation is visualized in Fig. 7 [case (c)] where the value $[N_{DD}]^i = [EL2]^i$ has also been drawn. The intersection of [EL2] and [Cr] shows that more than 90% of EL2 is ionized. This observation justifies the previous approximation $N_{DD}^i = N_{DD}$ for high Cr cases.

2. GaAs slightly doped with Cr ($[Cr] \leq 10^{16} \text{ cm}^{-3}$)

The Cr concentration can still be evaluated from optical absorption measurement. But, for such concentrations lower than 10¹⁶ cm⁻³, the result is not accurate. In fact, the samples C1 and C2 given in Table III have been cut in the seed side of two Bridgman ingots. It has been proved¹⁵ that the Cr concentration in the seed side of ingot varies linearly with the Cr doping, the segregation coefficient being equal to 8.9 × 10⁻⁴ in our experimental growth conditions. The concentrations reported in Table III have thus been deduced from the Cr doping of the ingots and are reliable.

Figure 8 gives the Shockley diagram with the Cr level and the deep donor EL2. We have neglected on Fig. 8 the shallow acceptors, their concentration being distinctly lower than that of Cr, as discussed above. Shallow donors have also been neglected, since this material C1 was grown with oxygen doping and expected to present a low N_D concentration. It is clear from Fig. 8 that if the ratio of concentrations

TABLE IV. Results from Hall effect measurements and optical absorption measurement on semi-insulating materials doped with Cr concentration ranging between 10^{16} and 10^{17} cm^{-3} .

Material	Optical absorption data		Hall effect data		
	Concentration of chromium (cm^{-3})	$(qR_H)^{-1}$ at 400 °K (cm^{-3})	μ_H at 400 °K ($\text{cm}^2/\text{V s}$)	slope of $\ln(R_H T^{3/2})^{-1}$ (eV)	Concentration of silicon (cm^{-3})
D1 Bridgman	3.5×10^{16}	1.5×10^{10}	1600	0.762	0
D2 LEC	3.5×10^{16}	7.5×10^9	1800	0.762	0
D3 Bridgman	5×10^{16}	1.2×10^{10}	2800	0.700	a few $\times 10^{16}$
D4 Bridgman	3×10^{16}	7.0×10^9	3200	0.757	$(1-2) \times 10^{16}$
D5 LEC	9×10^{16}	1.6×10^{10}	760	0.716	0
D6 LEC	9×10^{16}	8×10^9	1200	0.776	0

$[\text{EL2}]/[\text{Cr}] \geq 3-4$, then the neutral condition corresponds to a Cr level almost completely ionized. In other words, it brings back a previous case, already studied in paragraph II for the very-high-resistivity materials A9 and A10 with $(qR_H)^{-1} < 5 \times 10^{10} \text{ cm}^{-3}$ at 400 °K. The compensation results from the presence of the deep donor and of acceptors completely ionized (here the Cr level). The slope of the Arrhenius plot of $(qR_H T^{3/2})^{-1}$ is close to 0.759 eV, the enthalpy of ionization of EL2, as expected from Eq. (6). Furthermore, a high value of the true electron mobility is expected, let us say 4500–5000 $\text{cm}^2/\text{V s}$, since [Cr] is lower than 10^{16} cm^{-3} (see Fig. 2 and the values of μ_H obtained for materials A1–A3). It can be concluded that the Hall mobility is an apparent value, which is reduced according to Eq. (13), as for materials A9 and A10. We have previously observed (see Fig. 3) that the Hall mobility is reduced if the ratio $[\text{EL2}]/N_A$, i.e., $[\text{EL2}]/[\text{Cr}]$ in our case, is lower than 4. Combining this inequality with the previous one, we find

$$[\text{EL2}]/[\text{Cr}] \simeq 2-3, \text{ for materials C1 and C2}$$

and then

$$[\text{EL2}] \simeq (1-2) \times 10^{16} \text{ cm}^{-3},$$

which is a value very comparable to the value found in the previous different materials.

3. GaAs doped with intermediate concentration of Cr

This is the case where the concentrations of chromium, of the deep donor EL2, and eventually of shallow donors, are comparable (see Table IV). It is still easy to determine the Cr concentration from optical absorption measurements, but the concentration of EL2 or N_D can only be approximated. The concentration of silicon, as well as of any other shallow donor impurities has been evaluated for some samples from spark source mass spectroscopy. More generally, a crude estimation of N_D can be done, depending on whether the material is doped with shallow donor impurities or expected to be polluted with silicon or not (this last case corresponding to a Bridgman growth with oxygen overpressure, or an LEC growth). The interpretation of the electrical properties of these materials is thus difficult, but some conclusions can be drawn without ambiguity.

The slope of the Arrhenius plot of $(qR_H T^{3/2})^{-1}$ must be very close to 0.786 eV, which is half the enthalpy of the band gap at 400 °K.²⁵ In all the samples D, reported in Table IV, the resistivity is very high $[(qR_H)^{-1} < 2 \times 10^{10} \text{ cm}^{-3}$, at 400 °K] and thus the Fermi level is very deep. More precisely, in all the cases, one can observe that the Fermi level is locked between EL2 and Cr (see Fig. 9). This is due to the fact that the Cr level is always located above the deep donor EL2, at any temperature, since we have from Eqs. (6) and (9),

$$E_C - E_T(\text{EL2}) = 0.759 - 2.37 \times 10^{-4} T \text{ eV}$$

$$(g_{DD} = 1),$$

where $g_{DD} = g_0/g_1$ for EL2. and

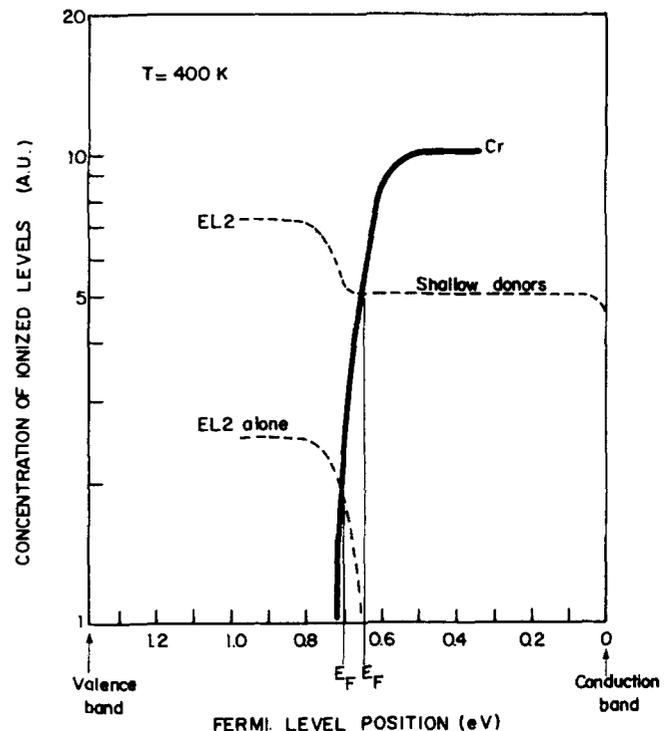


FIG. 9. Shockley diagram corresponding to a semi-insulating GaAs with a given concentration of the deep Cr acceptor and the deep donor EL2, with or without shallow donors.

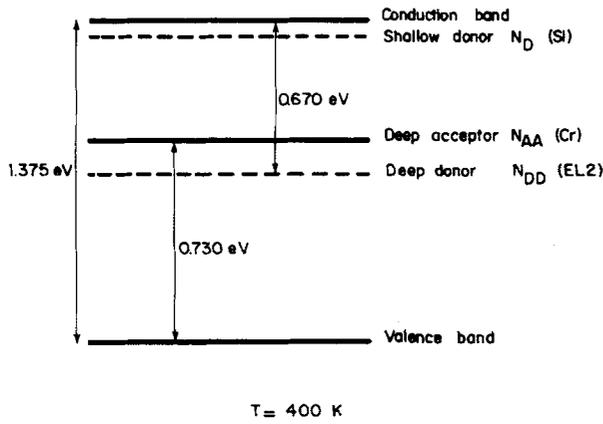


FIG. 10. Scheme of the band gap with the different important levels, at 400°K.

$$E_C - E_T(\text{Cr}) = [E_G - E_T(\text{Cr}) - E_V] \\ = 0.759 - 2.4 \times 10^{-4} \frac{T^2}{T + 204} \quad (g_{AA} = 0.93),$$

where $g_{AA} = g_0/g_1$ for the Cr level. Thus

$$E_C - E_T(\text{EL2}) > E_C - E_T(\text{Cr}) \quad \text{for any } T. \quad (28)$$

The scheme of the levels at 400°K is drawn in Fig. 10. The Fermi level, being pinched between the two levels, is close to $\frac{1}{2}E_G(T)$ with

$$E_G(T) = \Delta H(T) - T\Delta S(T). \quad (29)$$

Since the variation of E_G at high temperature is almost linear, the slopes of the Arrhenius plot of $(R_H T^{3/2})$ will be just equal to half ΔH (400°K), i.e., 0.786 eV. Indeed, similar values are always observed in this kind of materials (see Table IV).

But it can be concluded that the slope S is not a very useful parameter for the diagnostic, since very similar val-

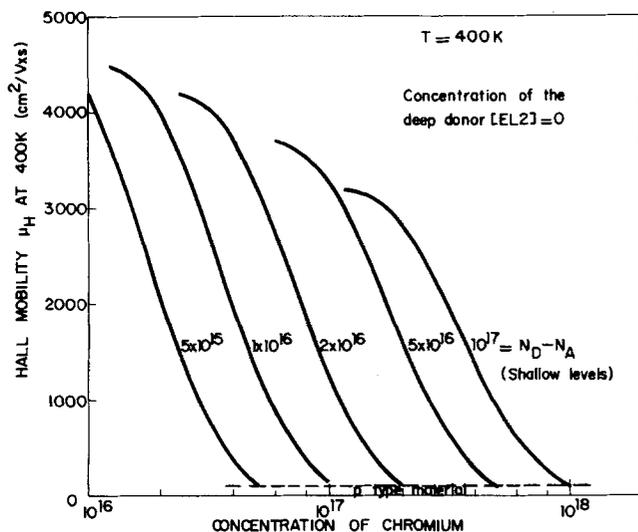


FIG. 11. Expected variation of the observed Hall mobility in semi-insulating GaAs, as a function of the Cr concentration, for different values of $N_D - N_A$ (the concentrations of shallow donors and acceptors), assuming that the concentration of the deep donor EL2 is zero.

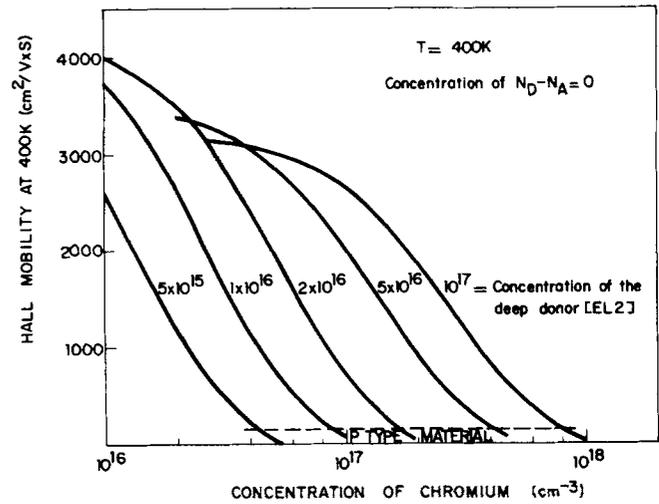


FIG. 12. Expected variation of the observed Hall mobility in semi-insulating GaAs, as a function of the concentration of chromium, for different concentrations of the deep donor EL2, assuming that $N_D - N_A$ of shallow levels is zero.

ues, $\frac{1}{2}\Delta H$ (gap) or ΔH (EL2), are measured in two extreme cases.

Our analysis of each level has shown that the Cr level is located above the EL2 level in the gap. This is actually confirmed by the observation that non-Cr-doped material can be as resistive as Cr-doped material (see for instance A2, A9, and A10 in Table I, compared to B1–B4 in Table II). This means that the Fermi level E_F is located at the same position in the two cases. But the deep donor is necessarily below E_F , while the deep Cr acceptor is above E_F (see Fig. 9 for instance).

The observed mobilities are reduced according to Eq. (13), since the Fermi level is very deep. As is clearly seen in Fig. 9, the smaller the concentration of shallow donors, the deeper the Fermi level, the lower the mobility. This conclu-

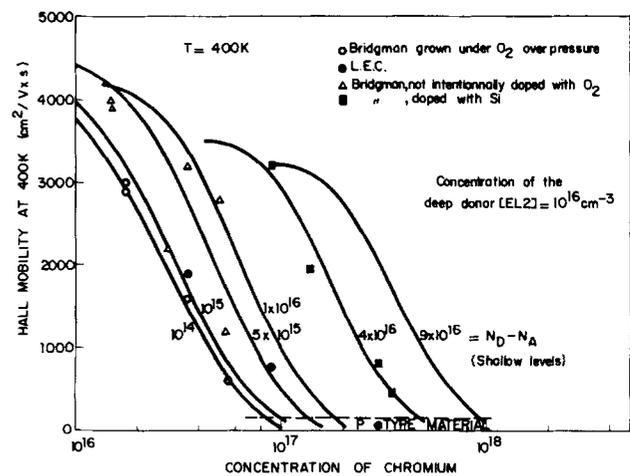


FIG. 13. Expected variation (full lines) of observed Hall mobility in semi-insulating GaAs, as a function of the concentration of chromium, for different values of $N_D - N_A$ (the concentration of shallow donors and acceptors), and for a given concentration of the deep donor EL2 equal to 10^{16} cm^{-3} . Points corresponding to experimental results on different materials described in Tables II and IV are also reported.

sion is quite coherent with the observations reported in Table IV. In materials D1, D2, and D5, where N_D is negligible, μ_H decreases in a large way when Cr increases. At the opposite, in materials D3 and D4, where $N_D = [\text{Si}] \simeq \text{a few } 10^{16} \text{ cm}^{-3}$ (due to slight doping with Si), μ_H is larger than in materials D1 and D2, although doped with an equal or larger Cr concentration.

4. Global assessment of any Cr-doped materials

After having studied each case in detail, it seems of practical interest to give some tools to assess any slice of Cr-doped GaAs in a simple and routine way. For this purpose, we have generated sets of curves giving the Hall mobility measured on semi-insulating materials as a function of the Cr concentration, which can be determined from optical absorption measurements.

The equation (24) of neutrality can be solved generally taking into account the shallow levels with both deep donor and acceptor levels:

$$N_D + [\text{EL2}]^i = N_A + [\text{Cr}]^i$$

or

$$N_D + [\text{EL2}][1 - f(\text{EL2})] = N_A + [\text{Cr}]f(\text{Cr}),$$

where $f(\text{EL2})$ and $f(\text{Cr})$ are given by Eqs. (1) and (10). Developing this expression, one obtains the following equation, the variable being $y = \exp[(E_C - E_F)/kT]$:

$$ay^2 + by + c = 0, \quad (30)$$

where

$$a = N_D + [\text{EL2}] - N_A \exp[(E'(\text{Cr}) - E_G)/kT], \quad (31)$$

$$b = N_D + [\text{EL2}] - N_A - [\text{Cr}] + (N_D - N_A) \times \exp\left(\frac{E'(\text{EL2}) - E_G + E'(\text{Cr})}{kT}\right), \quad (32)$$

$$c = (N_D - N_A - [\text{Cr}]) \exp[E'(\text{EL2})/kT], \quad (33)$$

$E'(\text{EL2})$, $E'(\text{Cr})$, and E_G being given by Eqs. (6), (9), and (11), respectively.

The Fermi level is obtained by solving Eq. (30), and thus n and p can be calculated. The Hall mobility is then deduced from Eq. (13), knowing the value of μ_{H_0} from Fig. 2 and assuming $\mu_n/\mu_p = 15$.

Figure 11 gives a first set of curves corresponding to variable values of $N_D - N_A$, the shallow levels, for a concentration of EL2 equal to zero. The true electron mobility μ_H is deduced from Fig. 2, taking the total concentration of ionized impurities equal to twice the value of $N_D - N_A$. Figure 12 gives another set of curves, corresponding to different values of $[\text{EL2}]$, for $(N_D - N_A) = 0$. It is interesting to note that there is only a slight difference between these two sets, which is due to the fact that the deep donor EL2 is almost completely ionized in most of the cases, as we already observed. This slight difference means also that the analysis may be ambiguous in some cases, since similar effects can be due to the presence of the shallow donors or to the deep donor.

Another set of curves has been computed which takes into account both the shallow levels and the deep donor (see Fig. 13). In this figure, the curves correspond to a fixed con-

centration $[\text{EL2}] = 10^{16} \text{ cm}^{-3}$ and to different values of $N_D - N_A$. Experimental points, corresponding to materials of Tables II and IV, have also been reported. A remarkable agreement is found. The curve corresponding to $(N_D - N_A) = 4 \times 10^{16} \text{ cm}^{-3}$ fits the materials doped with silicon. Oppositely, all the materials grown with oxygen fit in with curves corresponding to values of $(N_D - N_A)$ lower than 10^{15} cm^{-3} . These last curves are almost superimposed, since, in this case, the reduced mobility is due to only the presence of EL2. Furthermore, Fig. 13 clearly shows that the concentration of EL2 is around 10^{16} cm^{-3} in these materials. Czochralski materials also correspond to low values of $(N_D - N_A)$. Lastly, Bridgman materials not intentionally doped with oxygen show values of $(N_D - N_A)$ a bit larger, but rather scattered. It turns out that the set of curves, given by Fig. 13, can actually be a working tool to assess semi-insulating GaAs in a very direct way.

VI. CONCLUSION

Quite different semi-insulating GaAs materials have been investigated: undoped materials and materials doped with Cr concentrations up to $3 \times 10^{17} \text{ cm}^{-3}$. It has been shown that the shallow donors N_D and acceptors N_A are compensated by the deep donor EL2 and the deep acceptor related to chromium. The most important result of this work is that the combination of the Hall measurements with the optical absorption measurements, allows us to obtain a detailed characterization of semi-insulating GaAs, yielding, besides the Cr concentration the concentration of the deep donor EL2 and $(N_D - N_A)$, the difference between the concentration of shallow donor and acceptor levels.

All the conclusions concerning each type of material are reported in Table V. In the case of Cr-doped materials, the set of curves given in Fig. 13 can actually be used to assess any piece of material in a straightforward way.

Lastly, the conclusions obtained for each type of material lead to the following general remarks.

The concentration of the deep donor EL2 has been determined in several types of materials to be close to 10^{16} cm^{-3} , typically $(1-2) \times 10^{16} \text{ cm}^{-3}$. More generally, it seems to be equal to this value, whatever the type of material, Bridgman or Czochralski, doped with oxygen or not. This observation confirms the result already obtained elsewhere, following which this deep donor is not related, directly or indirectly to the presence of oxygen.

The concentration of shallow acceptors seems to be low in our conditions of Bridgman growth. It is generally below $5 \times 10^{15} \text{ cm}^{-3}$.

The results are consistent with a decrease of shallow donors due to the presence of oxygen during the growth, especially in Bridgman crystals.

In most of the cases, the activation energy of $1/R_H$ [the slope of the Arrhenius plot $(R_H T^{3/2})^{-1}$] is very close to 0.76 eV. This value corresponds either to the enthalpy of ionization of the deep level EL2, or to half the enthalpy of the energy gap at 400 °K. This parameter does not help significantly for the characterization of usual semi-insulating GaAs ingots. Oppositely, the Hall mobility and the sign of

TABLE V.

Cr concentration (from optical absorption) (cm ⁻³)	Hall data (400 K)			Compensation		Remarks	
	Type	$\frac{9}{R_H}$ (cm ⁻³)	slope of $\ln\left(\frac{1}{R_H T^{3/2}}\right)$ $= f\left(\frac{1}{T}\right)$ (eV)	Hall mobility μ_H (cm ² /V s)	Compensation ratio (given by Fig. 1 or 3)		Compensation levels (cm ⁻³)
Undoped Cr = 0	<i>n</i>	$> 2 \times 10^{10}$	$\approx 0.76 = \Delta H$ (EL2)	$\mu_H > 4500$ True mobility of electrons	$\frac{[\text{EL2}]}{N_A - N_D} > 4$	$N_A - N_D \approx 10^{15}$	Total number of ionized levels $N_T' < 3 \times 10^{15}$ N_T' given by Fig. 2
	<i>n</i>	$> 5 \times 10^{12}$	$0.35 - 0.42 = \frac{1}{2}\Delta H$ (EL2)	$2000 < \mu_H < 4000$ Reduced mobility due to inhomogeneity effects	$\frac{[\text{EL2}]}{N_A - N_D} > 1$	$N_A - N_D < 10^{13}$	$[\text{EL2}] = \text{some} \times 10^{16}$ $N_A < 10^{15}$
	<i>n</i>	$< 2 \times 10^{10}$	$\approx 0.76 = \Delta H$ (EL2)	$\mu_H < 4000$ Reduced mobility due to deep Fermi level True mobility ≈ 5000	$\frac{[\text{EL2}]}{N_A - N_D} < 4$ (ratio given by Fig. 3)	$N_A - N_D = \text{some} \times 10^{15}$	$[\text{EL2}] = \text{some} \times 10^{16}$ $N_A = \text{a few} \times 10^{15}$
$[\text{Cr}] < 10^{16}$	<i>n</i>	$< 2 \times 10^{10}$	$\approx 0.76 = \Delta H$ (EL2)	$\mu_H < 4000$ Reduced mobility due to deep Fermi level True mobility ≈ 5000	$\frac{[\text{EL2}]}{[\text{Cr}] + N_A - N_D} < 4$ (ratio given by Fig. 3)	$[\text{Cr}] + N_A - N_D \approx [\text{Cr}]$	$[\text{Cr}] < [\text{EL2}]$ $[\text{EL2}] = \text{some} \times 10^{16}$ $N_A + [\text{Cr}] = \text{a few} \times 10^{15}$
$10^{16} < [\text{Cr}] < 10^{17}$	<i>n</i>	$< 2 \times 10^{10}$	$\approx 0.78 = \frac{1}{2}\Delta H$ (Gap)	$\mu_H < 2000$ Reduced mobility due to deep Fermi level True electron mobility ≈ 4000	$\frac{[\text{Cr}]}{[\text{EL2}] + N_D - N_A} \approx 6$	$N_D - N_A$ given by Fig. 13	
	<i>n</i>	$< 2 \times 10^{10}$	$\approx 0.78 = \frac{1}{2}\Delta H$ (Gap)	$2000 < \mu_H < 3000$	$\frac{[\text{Cr}]}{[\text{EL2}] + N_D - N_A} \approx 3$	$\text{EL2} + N_D - N_A$ given by Fig. 13	N_D possibly large (Si pollution expected)
	<i>n</i>	$< 2 \times 10^{10}$	$\approx 0.78 = \frac{1}{2}\Delta H$ (Gap)	$100 < \mu_H < 2000$ Reduced mobility due to deep Fermi level True electron mobility $\approx 3000 - 3500$	$\frac{[\text{Cr}]}{[\text{EL2}] + N_D - N_A} < 10$	$[\text{EL2}] + N_D - N_A$ given by Fig. 13	$[\text{EL2}] + N_D = \text{a few} \times 10^{16}$
$[\text{Cr}] > 10^{17}$	<i>p</i>	$\rho > 10^5 \Omega \text{ cm}$	slope of $\rho T^{3/2}$ $0.78 = \frac{1}{2}\Delta H$ (Gap)	$\mu_H \# 100$ True electron mobility ≈ 3000	$\frac{[\text{Cr}]}{[\text{EL2}] + N_D - N_A} > 10$		$[\text{EL2}] + N_D \approx [\text{EL2}] = \text{some} \times 10^{16}$

the Hall constant are the Hall data giving the most useful information. It has been seen that, in most of the cases, and even in the case of slightly Cr-doped material and some undoped materials, μ_H is an apparent, reduced mobility. An estimation of the true value of the electron mobility at 400 °K has been based on experimental data, and this value has been reported in Table V. As a matter of fact, it is clear that the Hall mobility, measured on *n*-type layers obtained by implantation in the semi-insulating materials studied above, should be high, i.e., of the order of 4000 cm²/V s, even in materials with rather large Cr concentration.

This work has contributed to clarify the compensation in GaAs. It should allow the determinations of which kind of material is needed in the different technologies used for making microwave GaAs devices, such as FET's or integrated circuits.

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- ¹N.G. Ainslie, S.E. Blum, and J.F. Woods, *J. Appl. Phys.* **33**, 2391 (1962).
²J.M. Woodall and J.F. Woods, *Solid State Commun* **6**, 597 (1963).
³C.H. Gooch, C. Hilsum, and B.R. Holeman, *J. Appl. Phys.* **32**, 2069 (1961).
⁴G.R. Cronin and R.W. Haisty, *J. Electrochem. Soc.* **111**, 874 (1964).
⁵J.F. Woods and N.G. Ainslie, *J. Appl. Phys.* **34**, 1469 (1963).

- ⁶T. Shimoda and S.I. Akai, *Jpn. J. Appl. Phys.* **8**, 1352 (1969).
⁷S.J. Bass and P.E. Oliver, International Symposium on GaAs, 1966, p. 41 (unpublished).
⁸M.E. Weiner, D.T. Lassota, and B. Schwartz, *J. Electrochem. Soc.* **118**, 305 (1971).
⁹E.M. Swiggard, S.H. Lee, and F.W. von Batchelder, International Conference on GaAs, 1976, Int. Phys. Conf. Ser. n° 33b, 1977, p. 23 (unpublished).
¹⁰R.W. Haisty, E.W. Mehal, and R. Stratton, *J. Phys. Chem. Solids* **23**, 829 (1962).
¹¹J. Blanc and L.R. Weisberg, *Nature, (London)* **192**, 155 (1961).
¹²R. Zucca, *J. Appl. Phys.* **48**, 1987 (1977).
¹³P.F. Lindquist, *J. Appl. Phys.* **48**, 1262 (1977).
¹⁴D.C. Look, *J. Appl. Phys.* **48**, 5141 (1977).
¹⁵G.M. Martin, M.L. Verheijke, JAJ Jansen, and G. Poiblaud, *J. Appl. Phys.* **50**, 467, (1979).
¹⁶G.M. Martin and D. Bois, Spring Meeting of the Electrochemical Society, 1978, Proceedings of the Topical Conference on Characterization Techniques, Vol. 78-3, p. 32 (unpublished).
¹⁷G.M. Martin, A. Mitonneau, and A. Mircea, *Electron. Lett.* **13**, 191 (1977).
¹⁸H.I. Ralph, *J. Appl. Phys.* **49**, 672 (1978).
¹⁹G.M. Martin, A. Mitonneau, D. Pons, A. Mircea, and D.W. Woodard, *J. Phys. C* (to be published).
²⁰A. Mitonneau, A. Mircea, G.M. Martin, and D. Pons, *Rev. Phys. Appliquée (France)* **14**, 853 (1979).
²¹D. Pons, thesis, Université de Paris VI, April, 1979.
²²A. Mircea, A. Mitonneau, L. Hollan, and A. Briere, *Appl. Phys.* **11**, 153 (1976).
²³A.M. Huber, N.T. Linh, M. Valladon, J.C. Debrun, G.M. Martin, A. Mitonneau, and A. Mircea, *J. Appl. Phys.* **50**, 4022 (1979).
²⁴A. Mircea and A. Mitonneau, *J. Phys. Lett. (France)* **40**, L31, (1979).
²⁵C.D. Thurmond, *J. Electrochem. Soc.* **122**, 1133 (1975).
²⁶L.J. Van der Pauw, *Philips Res. Rep.* **13**, 1-9 (1958).
²⁷C. Herring, *J. Appl. Phys.* **31**, 1939 (1960).
²⁸P. Blood and J.W. Orton, *Rep. Prog. Phys.* **41**, 157 (1978).
²⁹W. Shockley, *Electrons and Holes in Semi-conductors* (Van Nostrand, Amsterdam, 1950), p. 465.
³⁰B. Clegg (private communication).