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Deep hole traps in p-type GaSe single crystals

C. Manfredotti, R. Murri, and A. Rizzo
Istituto di Fisica, Universita di Bari, Bari, Italy

S. Galassini and L. Ruggiero
Istituto di Fisica, Universita di Lecce, Lecce, Italy
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Space-charge-limited-current measurements have been performed at room temperature on GaSe single crystals. The samples investigated were p type and were grown from the melt by using the Bridgman-Stockbarger method. Three well-defined deep-lying hole traps have been found at 0.421, 0.465, and 0.543 eV above the valence band, respectively, and with concentrations ranging between 10^{12} and 10^{13} cm^{-3}. Their capture cross section has been found to be of the order of 10^{-12} cm^2, i.e., large enough to classify these traps as "giant traps." The origin and the nature of these centers is discussed and their possible connections with crystallographic, electrical, and optical properties of GaSe are extensively investigated.

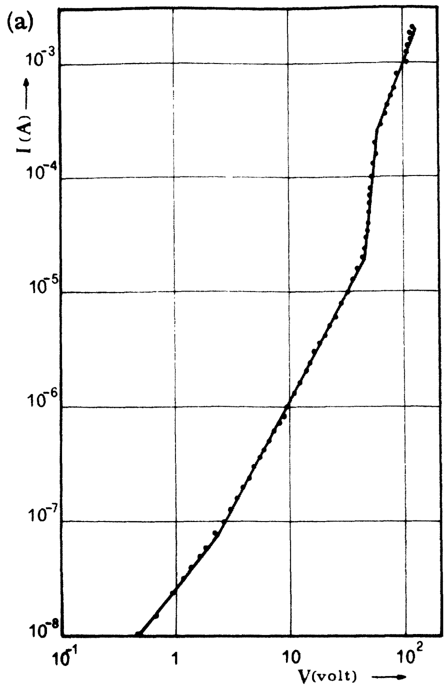
I. INTRODUCTION

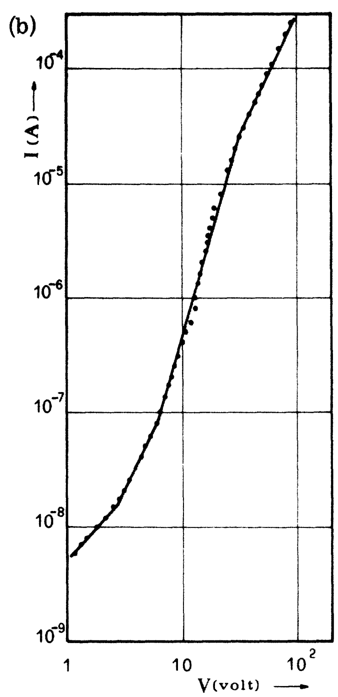
Gallium selenide is a very interesting compound, particularly from a fundamental point of view, because of its anisotropy in optical[1] and electrical[2] properties. However, it must be noted that investigations have been carried out so far essentially on its optical behavior in the exciton region,[3] and that its electrical properties are relatively poorly known.[4] In particular, nothing has been reported till now on deep trapping centers, which are known to affect greatly both optical and electrical properties. In this paper, we intend to cover these shortcomings, by measuring all the important trap parameters by means of the space-charge-limited-current (SCLC) method, which represents an invaluable tool for determining low concentrations and energy distributions of trapping centers in insulators.[5] These measurements have been made with current flowing along the c axis, i.e., across the layers, being GaSe, as it is well known,[6] a layer compound with thin tightly bound layers stacked on top of each other. The samples investigated were p type and were grown from the melt by using the Bridgman method. Three well-defined trapping levels have been found at 0.421, 0.465, and 0.543 eV from the valence band, respectively, and with concentrations ranging between 10^{12} and 10^{13} cm^{-3}. These traps do not appear simultaneously in the same sample: at most, two of them are present. Their capture cross section is of the order of 10^{-12} cm^2, i.e., large enough to classify these traps as "giant traps"[7]; therefore their presence can probably be correlated with the dislocations or impurities existing between the layers. In order to apply the SCLC method, the problem of measuring the hole drift mobility along the c axis had to be solved, since this mobility was not previously known. This determination was made directly by using the transit-time technique (TTT) with bursts of 40-keV electrons[8] and with α particles.[9] The high value which was found for this mobility (215 cm^2 V^{-1} sec^{-1}) raises questions about the effective (or intrinsic) anisotropy of the electrical properties of GaSe.

II. EXPERIMENTAL

The GaSe crystals have been grown in our laboratory from the melt by using the Bridgman-Stockbarger method, according to a special procedure described elsewhere.[10] In this particular case, the silica crucible (180 mm length and 10 mm inside diameter) was loaded with 0.1 mole of Ga and Se (purity 99.999%). The charge was slowly heated up to 1050 °C and kept at this temperature for 15 h in order to complete the reaction. The GaSe compound so obtained was then allowed to crystallize by moving the crucible through a temperature gradient of 30 °C/cm at a lowering rate of 1 mm/h. Analysis performed with x-ray diffraction proved the ingots to be single crystals, while stoichiometry was accurately checked by means of atomic absorption spectrometry.

Samples were cut in squares of 1 cm^2 and gently cleaved in order to avoid as far as possible introducing dislocations. Their thickness ranged from 50 to 300 μm along the c axis, and was accurately determined with an optical microscope. An electrical analysis carried out by means of the Van der Pauw method,[11] showed the samples to be p type, with a resistivity of about 10^5 Ω cm and a mobility of 40 cm^2 V^{-1} sec^{-1} along the layers. Evaporated In contacts were used with an area of 7 mm^2. A slight diffusion was carried out in an infrared oven at 300 °C under N_2 atmosphere in order to improve the Ohmicity: in effect, I-V characteristics previously checked with a curve





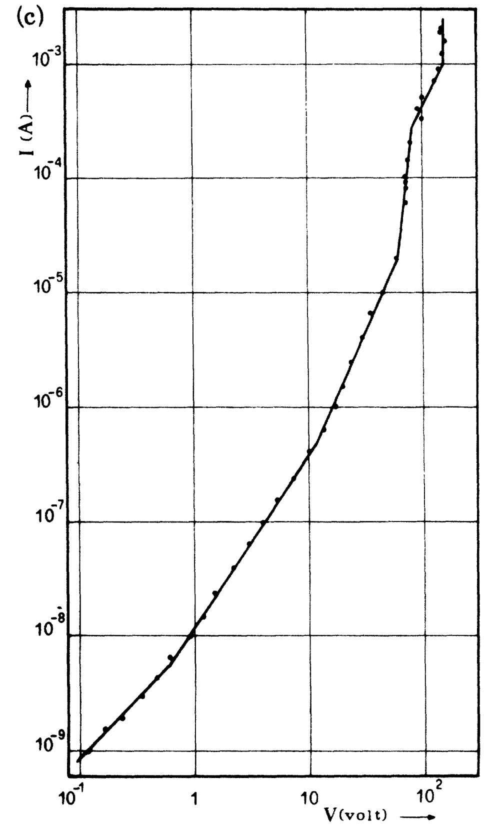


FIG. 1. log-log plot of the steady-state current vs voltage characteristics at room temperature for a sample indicating the presence of: (a) a discrete trapping level, (b) a diffuse trapping level, and (c) two discrete trapping levels.

tracer were strictly Ohmic at low voltages and showed a symmetrical behavior with respect to the voltage polarity. We measured the steady-state I-V characteristics on about 30 different samples extracted from three different ingots. Measurements were repeated about five times on the same sample and with both polarities: No significant differences were ever found between the corresponding results. Since we were interested only in deep traps, we report here only data obtained at room temperature: Results obtained at lower temperatures and concerning relatively shallow traps will be reported in a future publication. The experimental apparatus is described elsewhere.[12] Typical I-V curves are illustrated in Fig. 1. Figure 1(a) clearly corresponds to a discrete trapping level,[13] because of the long quadratic region following the Ohmic one. The vertical region is certainly due to the complete filling of the traps (trap-filled limit or TFL), according to the theory,[13] and not to other effects such as Joule heating, electrical breakdown, etc., since the curve keeps on with a superquadratic slope, probably due to another level. Anyhow, we limited ourselves to currents not larger than few mA, in order to avoid local Joule heating, and we took into account only curves with well defined TFL. Figure 1(b) shows a clear example of a diffuse trapping level,[14] because of the short quadratic region and of the long superquadratic one (slope 3.6). According to the theory, the traps

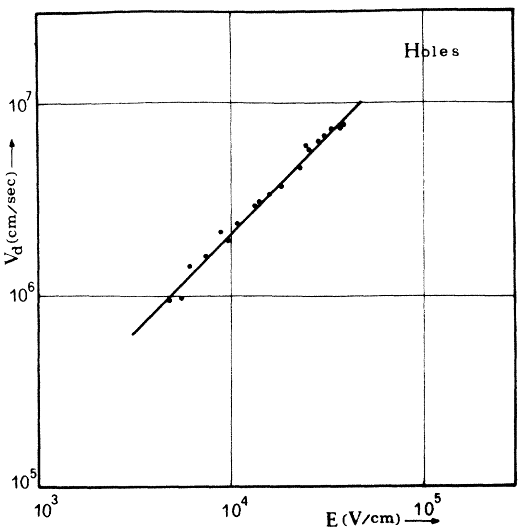


FIG. 2. Hole drift velocity as a function of the electric field at room temperature, as measured by the time-of-flight method.

should have a double-exponential or "cusp" like energy distribution, with an energy width of 0.135 eV. Curves of type 1(b) were in number less than half than type 1(a). Finally, Fig. 1(c) shows a very interesting example of a double discrete level, which is rarely found in the literature.

In order to apply the SCLC theory consistently, hole drift mobility along the c axis must be known.[13] Since we might reasonably expect this mobility to be very low,[15] and since the usual Hall method is not suitable for GaSe because of its layer structure, we chose the transit-time technique,[16] which is the best direct method for determining the drift mobility. Measurements were carried out with a 40-keV pulsed electron accelerator[8] and using ^{241}Am α particles of 5.47 MeV.[9] Gold evaporated electrodes were used in this case in order to keep carrier injection as low as possible. The drift velocity obtained with this method is shown in Fig. 2 as a function of the applied electric field. One can see that these measurements cover exactly the range of electric field used in SCLC curves, and that drift velocity is strictly proportional to the electric field in this range. The hole drift mobility turns out to be unexpectedly high, if one takes into account the strongly anisotropic structure of GaSe: 215 cm^2 V^{-1} sec^{-1}. From the measurements carried out with α particles, we obtained also the mobility-trapping-time product $\mu\tau^+$, 1.36×10^{-6} cm^2 V^{-1}, from which one can get a trapping time of about 6×10^{-9} sec.

The valence-band density of states was determined by measuring the temperature dependence of the Hall effect perpendicularly to the c axis, and applying the single-donor-single-acceptor model to the data obtained. Details will appear elsewhere.[17] Assuming a normal three-dimensional band, as supported by the mobility data, and a normal spin degeneracy, i.e., $g=2$, a fit of the experimental data gives a density-of-states effective mass of $0.57m_e$; from this a density of states $N_V = 1.08\times10^{19}$ cm^{-3} can be derived.

III. RESULTS

The I-V curves were analyzed according to methods described in some detail elsewhere.[12] The existence of three well-defined trapping levels was shown and the corresponding data are presented in Tables I–III. For the setting of these tables, the following criteria were applied: (1) The Lampert or discrete level method[13] was used whenever the quadratic region was long enough and the eventual superquadratic portion short enough to be consid-

TABLE I. Data on the level at 0.543 eV, as derived from the analysis of the I-V curves. [Note. E_L is the lower edge of the distribution, $2kT_c$ is its width, $E_L - 2kT_c$ is an estimate of the maximum of the distribution, H_{min} and H_{max} are the minimum and the maximum value of the total trap density for the case of the diffused level, while E_t and N_t are the trap depth and concentration in the case of discrete level.]

Sample	E_L (eV)	$E_L - 2kT_c$ (eV)	E_t (eV)	N_t (10^{12} cm^{-3})	H_{min} (10^{12} cm^{-3})	H_{max} (10^{16} cm^{-3})	$2kT_c$ (eV)
$G3$			0.555	10.9			
$G4$			0.548	6.94			
$G5$			0.538	1.16			
$G6$			0.529	1.85			
$G7$	0.672	0.537			0.52	0.15	0.135
$G9$			0.549	1.6			
$G10$	0.644	0.510	0.540	1.71	0.28	0.05	0.135
$G11$	0.581	0.503			0.19	8.03	0.078
$G14$	0.638	0.519	0.543	15.0	27.3	16.6	0.119
Average	0.634	0.517	0.543	5.53	7.07	6.21	0.117

TABLE II. Data on the level at 0.465 eV [Note. See Table I.].

Sample	E_L (eV)	$E_L - 2kT_c$ (eV)	E_t (eV)	N_t (10^{12} cm^{-3})	H_{min} (10^{12} cm^{-3})	H_{max} (10^{16} cm^{-3})	$2kT_c$ (eV)
*G*2	0.585	0.461	0.489	23.9	4.37	7.24	0.124
*G*3	0.639	0.474			27.4	0.83	0.166
*G*5			0.472	2.7			
*G*7			0.463	2.1			
*G*10	0.581	0.457	0.455	4.5	24.9	3.89	0.124
*G*13	0.635	0.453			56.1	0.83	0.181
*G*15			0.438	17.2			
*P*2			0.455	4.1			
*P*3			0.481	3.9			
Average	0.610	0.461	0.465	8.35	28.2	3.2	0.149

ered as a transition tract; (2) the Sworakowski-Pigȍn or diffused-level method was used in the opposite cases; (3) in ambiguous cases, both methods were applied; (4) every reported datum is an average between different measurements on the same sample; (5) curves not satisfying the quasi-Fermi level analysis or the V_{TFL} test (see Sec. IV) were rejected.

In these tables, the two methods quoted at the points 1 and 2 are reported together for comparison purposes. The symbols E_t and N_t refer to the density of traps in the case of a discrete level. For the diffused level, E_L is the lower edge of the energy distribution, $2kT_c$ its energy width, $E_L - 2kT_c$ the lowest position of the maximum of the energy distribution (since the highest one coincides with the valence band) and H_{min} and H_{max} are the minimum and the maximum value of the trap density, corresponding, respectively, to the preceeding positions of the distribution peaks.

Table I shows the results obtained for the deepest trapping level: One can observe the good agreement between the average values of E_t and $E_L - 2kT_c$, as well as between N_t and H_{min}. From this fact, one can easily conclude that the Lampert and the Sworakowski-Pigȍn methods practically coincide, as far as the more important characteristics of the traps are concerned. One can also observe the quite small fluctuations among the measurements on the various samples, a fact that, on the one hand witness for the excellence of the method and, on the other hand, for the electrical homogeneity of the Bridgman ingots used. These ingots had their axis along the layers and the different samples were cut from different positions along the ingot axis. Therefore, ingots were homogeneous both radially and longitudinally. Table II shows the results obtained for the intermediate trapping level. The conclusions are the same as before, except that in this case the agreement between N_t and H_{min} is worse, in spite of the very good agreement between E_t and $E_L - 2kT_c$.

Finally, Table III presents the results for the shallowest level, which occurs less frequently than the preceding ones and is probably an alternative position of the previous level.

These levels do not interfere with each other, since they do not appear all together in the same sample or, when two of them are present, at least one is a discrete one. The only exception seems to be *G*10, in which however H_{min} turns out to be extremely low (as in *G*8 and *G*11) so that the Sworakowski-Pigȍn model is not completely suitable. In effect, it is quite possible that, because of the criteria followed in deciding between models, some true single levels were mistaken for diffused ones. If this is true, since about one third of the levels turned out to be of the diffuse type, this should

TABLE III. Data on the level at 0.421 eV [Note. See Table I.].

Sample	E_L (eV)	$E_L - 2kT_c$ (eV)	E_t (eV)	N_t (10^{12} cm^{-3})	H_{min} (10^{12} cm^{-3})	H_{max} (10^{16} cm^{-3})	$2kT_c$ (eV)
*G*8	0.580	0.425	0.426	0.25	0.26	0.02	0.155
*G*10			0.406	1.7			
*G*11	0.560	0.420	0.440	0.83	0.69	0.04	0.140
*P*1	0.525	0.410	0.406	2.4	1.3	0.28	0.115
*P*4			0.426	1.6			
Average	0.555	0.418	0.421	1.16	0.75	0.11	0.136

mean that most of the levels are discrete. On the other hand, the Lampert interpretation gives rise to minor fluctuations in the data, and it is more self-consistent. It remains to remark that the "averages" in the tables are referred to the measurements and not to the samples. In conclusion, three trapping levels are evidenced, which are of the discrete type or, at the most, slightly diffuse in energy: the first one at 0.543 eV with a density of 5.5×10^{12} cm^{-3}, the second one at 0.465 eV with a density of 8.4×10^{12} cm^{-3}, and the third one at 0.421 eV with a density of 1.2×10^{12} cm^{-3}.

IV. DISCUSSION

A. Check for the "Lampert" interpretation

In this section we shall make a brief survey of the most important effects that, if present in I-V curves, could possibly be mistaken for SCLC effects. We shall prove that no such effect is present, and that the agreement between experimental data and predictions of the theory is completely satisfactory. These effects are (1) the Poole-Frenkel effect, which has been reported for GaSe at electrical fields higher than 10^3 V cm^{-1}.[18] It was quite impossible in our case to get a fit with the theory[19]: in any case our I-V curves, if interpreted as due to this effect above 10^3 V cm^{-1}, imply a dielectric constant which is one order of magnitude lower than the experimental one.[20] (2) For the same reasons, the Schottky effect[19] can also be excluded. This is an indirect proof of the quality of the injecting contacts. (3) Traps emptying[21] due to ionization should be rejected, since we observed the quadratic region and the electrode spacing to be always larger than the critical value[22] above which the quadratic region should disappear. (4) Double injection, which has been extensively reported for GaSe,[23] seems also to be discarded, since the shape of the I-V curves is quite different from what predicted from the theory and, as a matter of fact, no double injection theory is able to explain the superquadratic-quadratic transitions we observed in many I-V curves. Moreover, the electrodes were made of the same metal and, therefore, minority carrier injection could occur only by such mechanisms as tunneling or impact ionization. Investigations on double injection in GaSe are in progress; at the moment, it is reasonable to conclude that single carrier injection is the dominant mechanism in the range of currents investigated.

Checks with SCLC theory were carried out as follows: (1) According to the discrete-level SCLC theory,[13] the calculated electron quasi-Fermi level F_n at the end of the quadratic region should be equal to $E_t + kT$; this fact was verified with a reasonable approximation in all the cases we took into account. (2) According to the diffused level SCLC theory,[14] in the superquadratic region F_n should vary between $E_L + kT_c$ and $E_T - kT_c$, where E_T has been approximated with $E_L - 2kT_c$ (see Tables I–III). Curves not fulfilling the above criteria, which amounted to not more than a few percent of all cases, were discarded. (3) According to the SCLC theory,[13] V_{TFL} should be proportional to the square of the sample thickness d^2: this expectation is checked in Figs. 3(a), 3(b), and 3(c) for the three single levels at 0.543, 0.465, and 0.421 eV, respectively. The fluctuations are clearly due to errors in thickness measurements and to variations in trap concentration from sample to sample. Finally, the fact that holes were really the carriers injected in our samples, was checked by determining the conductivity type for relatively large currents (up to 10^{-3} A) by means of the Van der Pauw method.[11] Obviously, the current flow was along the layers in this case, but the injection mechanism should have been exactly the same. A clear p-type conductivity was established in all cases.

B. Origin and nature of traps

By making the reasonable hypothesis that the same traps are acting both in SCLC and in measurements of the mobility–trapping-time product, one can easily derive for these traps a cross section of 10^{-12} cm^2 from the measured value of the trapping time. This value, which incidently is just the same found for analogous electron traps in GaSe(I_2)[24] is clearly large enough to classify these traps as "giant traps,"[12] i.e., not associated to point defects, but to somewhat extended regions. These regions may well correspond to dislocations or stacking faults which are quite easy to produce in GaSe because of the weakness of the Van der Waals forces.[25] In effect, GaSe cleaves readily in the layer plane and its layers glide easily on top of each other, since dislocations in the layer plane are very mobile and the energy of the faults in the stacking sequence of the layers is very low. Clearly, these traps could be also attributed to impurities or "clusters" of impurities: In any case, it is more likely that they are segregated between layers, because of the structure of GaSe. The possible influence of these traps on electrical (e.g., mobility) and optical properties of GaSe is summarized in the following points: (1) The reduced mobility, by assuming a trapping-detrapping mechanism, should be equal to $\mu\theta$, where $\theta = n/n_t$, i.e., the ratio between free and trapped electron concentrations. In the present case, θ turns out to be 10^{-2}–10^{-3}, therefore one should expect a reduced mobility two or three orders of magnitude lower than 215 cm^2 V^{-1} sec^{-1}. Such low values have been reported elsewhere[26–28] for drift mobility

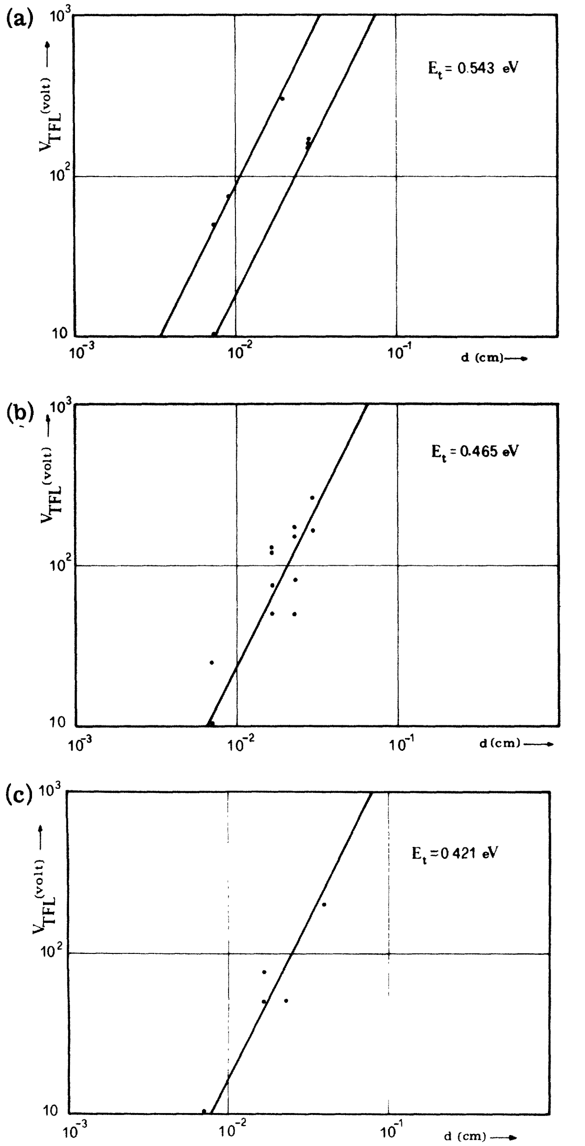


FIG. 3. Trap-filled limit voltage V_{TFL} vs electrode spacing for several samples and (a) for the level at 0.543 eV, (b) for the level at 0.465 eV, and (c) for the level at 0.421 eV. An average quadratic dependence is indicated (solid line).

along the c axis. In our case, clearly, detrapping is not present, since the transit times are in general less than the calculated detrapping times. In other cases, e.g., photovoltaic effect, etc., where rather low electric fields are present, the transit time is much longer and trapping-detrapping may easily occur. The detrapping time for the deeper-lying trap is about 10^{-5} sec, while for the other two it is one and two orders of magnitude lower, respectively. (2) Obviously, a reduced mobility can simulate a hopping mobility, because of the dependence of detrapping time on the energy depth of the traps. Hopping mobilities have been often reported for GaSe and some other layer structures along the c axis.[28,29] (3) Lifetime, which has been measured with different methods[27,30,31] and with different results, seems in average to be quite long and to imply a too large value of the photoconductive gain for GaSe (about 10^2–10^3 in the c direction), taking into account that GaSe is not a good photoconductor at room temperature. It may well be that this rather long lifetime is in fact simulated by detrapping. As an example, a lifetime of 4.3×10^{-6} sec has been measured for photoluminescence in GaSe[31]: This lifetime is surprisingly equal to our detrapping time. On the other hand, as it is well known for GaSe,[32] luminescence is much stronger in more disordered regions, i.e., in our hypothesis, with a higher concentration of traps.

V. CONCLUSIONS

Three deep-lying hole traps have been found in p-GaSe, at 0.543, 0.465, and 0.421 eV above the valence band, respectively. They are either discrete or slightly diffuse in energy, with an energy width around 0.1 eV. Their density is about 10^{13} cm^{-3} and their capture cross section is as large as 10^{-12} cm^2. As a consequence, these traps can be classified as "giant traps" and associated not to point defects but to somewhat extended regions, as dislocations or staking faults.

Moreover, these traps are expected to profoundly influence both electrical and optical properties of GaSe. In fact, the very low mobilities measured at low fields along the c axis should actually be "reduced" mobilities and, consequently, may also show an apparent hopping behavior. Such traps may simulate a rather long lifetime in GaSe by detrapping or play an important role in photoluminescence.

The SCLC model has been extensively tested in GaSe, both in its discrete and diffuse level formulation, and hole injection has been checked to be the only effect present in I-V curves, at least for currents lower than 10^{-3} A.

The hole drift mobility, measured along the c axis by transit-time method, has been found to be 215 $cm^2\,V^{-1}\,sec^{-1}$, i.e., larger than Hall mobility along the layers, which amounts to 40 $cm^2\,V^{-1}\,sec^{-1}$. Finally, together with mobility, also the hole density-of-states effective mass has been determined to be $0.57m_e$, corresponding to a density of states of 1.08×10^{19} cm^{-3} in the valence band.

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