Tin-related double acceptors in gallium selenide single crystals

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Gallium selenide single crystals doped with different amounts of tin are studied through resistivity and Hall effect measurements in the temperature range from 30 to 700 K. At low doping concentration tin is shown to behave as a double acceptor impurity in gallium selenide with ionization energies of 155 and 310 meV. At higher doping concentration tin also introduces deep donor levels, but the material remains p-type in the whole studied range of tin doping concentrations. The deep character of donors in gallium selenide is discussed by comparison of its conduction band structure to that of indium selenide under pressure. The double acceptor center is proposed to be a tin atom in interlayer position, with a local configuration that is similar to that of tin diselenide. The hole mobility exhibits an anomalous dependence on the tin content, attaining its maximum value in the ingot with 0.2% nominal tin content. This is proposed to be related to impurity pairing effects giving rise to thermal shallow acceptors with low ionization energy and low carrier scattering cross section, making the hole mobility to be controlled by phonon scattering mechanisms even for relatively high impurity content. © *1998 American Institute of Physics.* [S0021-8979(98)02909-0]

I. INTRODUCTION

Gallium selenide (GaSe) is a p-type semiconductor that belongs to the III–VI layered semiconductor family, which is characterized by a strong anisotropy in the chemical bonding. Each covalently bonded layer consists of four monoatomic sheets in the order Se–Ga–Ga–Se. The single layer is hexagonal and the c-axis is perpendicular to the layer plane. The layers are bound by weak van der Waals-type interactions. Several polytypes have been reported in the literature (β, γ, ϵ polytypes),[1,2] being the most common one that corresponds to ϵ polytype (D_{3h}^1 space group). The optical properties of GaSe are also anisotropic. Direct optical transitions between the top of the valence band and the minimum of the conduction band (at Γ point) are full allowed, if the electric field of the light is parallel to the c axis. For a perpendicular direction the transition is weakly allowed, due to spin-orbit coupling.[3] At room temperature (RT) the band gap of GaSe lies in the visible range ($E_g = 2.02$ eV).

The possibility of preparing GaSe high quality thin films through the so-called van der Waals epitaxy[4–7] has led to a renewed interest in this semiconductor due to its potential optoelectronic applications. In this issue, detailed information on doping processes plays an important role. The problem of doping, that was investigated early without drawing definitive conclusions,[8–13] has been recently approached by other groups that have specially studied the influence of impurities from groups I and II as acceptors in GaSe.[14–21] Room temperature hole concentrations of the order of 10^{15}–10^{16} cm^{-3} have been reported by doping with Cd,[17] Zn,[18] Cu,[19] and Ag.[20] Activation energies for hole concentration are of the order of 300 meV for Cd,[17] Zn,[18] or Mn[21] doped GaSe, of the order of 40 and 140 meV for Cu-doped samples,[19] and of the order of 60 meV for Ag-doped samples.[20] The highest ratio between hole concentration at RT and acceptor-impurity concentration has been attained in GaSe doped with nitrogen,[22] that turns out to be one of the most suitable acceptors in GaSe. Attempts to get low resistivity n-type GaSe have been up to now unsuccessful.[23–25]

As tin (Sn) is expected to behave as a donor impurity in GaSe when it substitutes for Ga, some authors have carried out studies on Sn-doped GaSe.[8,23–26] Nevertheless, the role played by Sn in the doping process of GaSe is not well understood yet. Photoluminescence measurements have been carried out recently in Sn-doped n-GaSe.[24] In those samples the photoluminescence spectra appear to be dominated by donor-vacancy complex centers. Hall effect (HE) measurements in Sn-doped p-GaSe reflect a highly compensated behavior with an activation energy of the acceptor level of some 100 meV[8] and the resistivity attains 2×10^7 Ω cm,[26] while in Sn-doped n-GaSe the activation energy of the donor level is of the order of 400[23] or 520 meV[25] and the resistivity attains up to 10^9 Ω cm.[23,25]

In this article we report on transport properties of GaSe single crystals doped with different amounts of Sn in the temperature range from 30 to 700 K. In Sec. II we describe the experimental setup. The results obtained on resistivity and HE measurements are shown in Sec. III. Section IV is devoted to the discussion on the role played by Sn as doping agent in GaSe and its influence on the transport properties of the material.

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TABLE I. Summary of the RT resistivity, carrier concentration ($c_{300\,K}$), and mobility for Sn-doped GaSe samples, compared to these found in the literature for n-type and p-type Sn-doped GaSe. Maximum hole mobility and the temperature value (T_{max}) at which it occurs are also included. The exponent of the temperature dependence of the hole mobility (γ) is also shown for temperature values at both sides of T_{max}.

Type	[Sn] (at. %)	$c_{300\,K}$ (cm^{-3})	$\rho_{300\,K}$ (Ω cm)	$\mu_{300\,K}$ (cm^2/V s)	μ_{max} (cm^2/V s)	T_{max} (K)	γ $T<T_{max}$	γ $T>T_{max}$	Ref.
	0.05	2.3×10^{15}	142	19.1	19.5	290	1.1	−0.7	
	0.1	4.1×10^{15}	50	30.4	66	145	1.2	−1.05	This
p	0.2	1.5×10^{16}	12	34.6	310	90	2.8	−1.8	work
	0.5	4.8×10^{13}	1.75×10^4	7.4	12	485	5.8	−0.7	
	0.01		1.0×10^3						Ref. 26
	0.05		1.7×10^7						
	0.05	1.2×10^{12}							Ref. 24
	0.1	2.1×10^{12}							
	0.5	1.6×10^{13}							
n	1	4×10^8	1.3×10^8						Ref. 25
	4	6×10^8	2×10^8						
	5		1.25×10^9						Ref. 23

II. EXPERIMENT

The GaSe crystals used in this study were grown by the Bridgman method from a stoichiometric melt of GaSe. Tin was introduced as pure element in a quantity to give 0.05, 0.1, 0.2, and 0.5 at % of Sn in the melt. As in Sn-doped InSe,[27] only a small part of the Sn remains in the GaSe crystal, the rest being rejected to the end of the ingot during the crystal growth process. The nominal amount of Sn added to the melt, hereafter denoted as [Sn], will be used to refer to each ingot. The growth system was technically improved as described in Ref. 22.

Square samples with faces perpendicular to the c axis were prepared from the ingots by cleaving and cutting with a razor blade. The interference fringe pattern in the infrared transmission spectrum was used to measure the thickness of the slabs, that ranged from 20 to 50 μm. Typical dimensions of the samples were 4×4 mm^2. Ohmic contacts for HE measurements were made by soldering with high-purity indium in the van der Pauw configuration.[28]

Low temperature HE was carried out in a helium closed cycle Leybold Heraeus cryogenic system. For HE measurements between 300 and 700 K the sample was heated in vacuum in a system implemented at the laboratory. The current flows along the layer plane and the magnetic field (0.6 T) was applied perpendicular to it. The linearity of the Hall and ohmic voltages on the injected current was checked out at each temperature.

III. RESULTS

Table I gives the typical values of the RT resistivity and hole concentration of samples from the ingots studied here compared to those of Sn-doped GaSe found in the literature. All the samples studied here appear to be p-type. The RT hole concentration and mobility increase with the Sn doping concentration attaining a maximum value for the 0.2% ingot and decreasing for the 0.5% ingot. Figure 1 shows the temperature dependence of resistivity for samples from each ingot analyzed here.

Figure 2 shows the temperature dependence of the hole concentration for several samples from the ingots used in this work as determined through

$$p=\frac{1}{|q|R_H}, \quad (1)$$

where q is the electron charge, and R_H is the Hall coefficient. The Hall factor has been assumed to be 1.[23,29] Let us point out several aspects of the temperature dependence of the hole concentration:

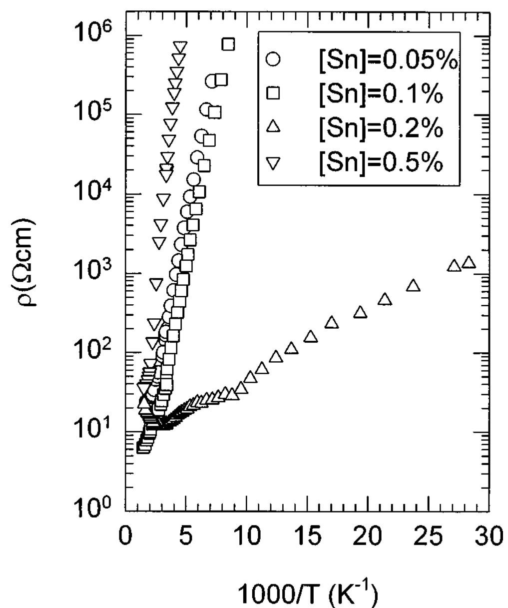

FIG. 1. The temperature dependence of the resistivity of Sn-doped GaSe. The nominal Sn doping concentration of the samples ([Sn]) is indicated in the figure.

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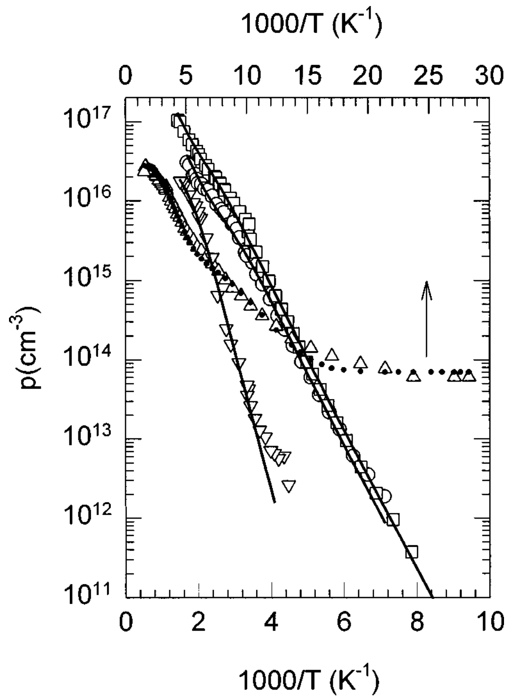

FIG. 2. The temperature dependence of the hole concentration of GaSe samples with [Sn]=0.05% (○), 0.1% (□), 0.2% (△), and 0.5% (▽). Solid and dotted lines correspond to fitting curves. Dotted fitting curve and experimental points measured for the sample doped with [Sn]=0.2% are referred to the upper x axis.

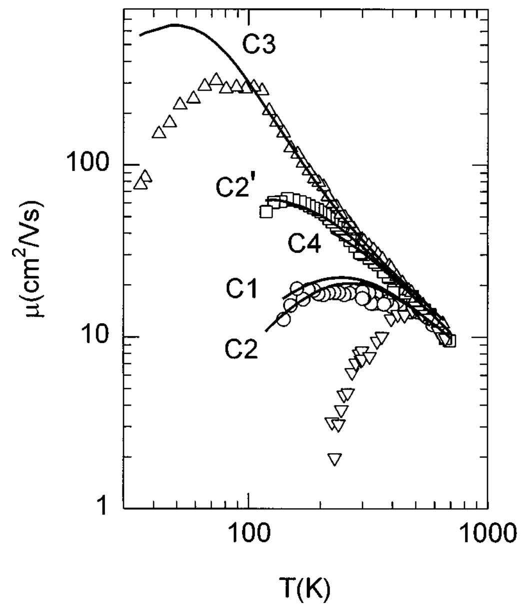

FIG. 3. The temperature dependence of the hole mobility of GaSe samples doped with different amounts of Sn. Experimental data from samples doped with [Sn]=0.05% (○), 0.1% (□), 0.2% (△), and 0.5% (▽). Curves C1, C2, C3, and C4 correspond to fitting curves to the above mentioned experimental data, respectively. Curve C2′ corresponds to a second fitting process of the experimental data from sample doped with [Sn]=0.1% in which a decrease of the effective concentration of ionized impurities is taken into account.

(i) The hole concentration is of the order of $2-3 \times 10^{16}$ cm^{-3} at 500 K for most samples, but for samples of GaSe doped with [Sn]=0.1%, in which no saturation effects are observed, the hole concentration is higher than 10^{17} cm^{-3} at the highest temperature values reached here.

(ii) The hole concentration exhibits an activated behavior with different activation energies. For the samples doped with [Sn]=0.05% and 0.1% the activation energy is 155 meV below 300 K. For samples doped with [Sn]=0.2% the activation energy is 155 meV above 210 K and 70 meV in the temperature range from 210 to 65 K. Below 65 K the hole concentration tends to reach a constant value of the order of 7×10^{13} cm^{-3}. For samples doped with [Sn]=0.5% the activation energy is 310 meV below 400 K. These samples also show the lowest RT hole concentration (Table I).

All these facts suggest that holes in Sn-doped GaSe are generated by the ionization of several acceptor levels, whose origin will be discussed in the next section.

Figure 3 shows the temperature dependence of the hole mobility for several samples from the ingots used in this work. A fact worth noting is that the highest RT hole mobility appears for samples doped with [Sn]=0.2% (Table I), that also exhibit the largest temperature range in which phonon scattering is the predominant mechanism.[22] At temperature values lower than $T_{\max}$ (Table I) impurity scattering mechanisms become dominant. In samples in which the hole mobility could be measured in a wide temperature range below $T_{\max}$ the exponent of its temperature dependence (γ) (Table I) was higher than that related to ionized impurity mechanisms ($\gamma=3/2$).

IV. DISCUSSION

Tin behaves as a shallow donor impurity in InSe.[30–32] From results reported in the previous section and those of other authors it seems that this is not the case in GaSe. Tin-doped n-GaSe exhibits very high resistivity values and the activation energy of the electron concentration is of the order of 400 meV[23] or 520 meV.[25] In Sn-doped p-GaSe various activation energy values have been observed. First, let us try to give an account of the temperature dependence of the hole concentration through a model including several acceptor levels with different ionization energy (E_{ai}) and compensating donor impurities, ruled by the equation[33]

$$p+N_d=\sum_{i=1}^{i=n}\frac{N_{\mathrm{ai}}}{1+\dfrac{\beta_i p}{N_v}\exp\left(\dfrac{E_{\mathrm{ai}}}{k_B T}\right)}, \tag{2}$$

where p is the hole concentration, k_B is the Boltzmann constant, T is the absolute temperature, N_d is the donor impurity concentration, n is the number of acceptor levels considered in each sample, N_{ai} is the concentration of each acceptor impurity, β_i are the degeneracy factors, and N_v is the density of states of the valence band that can be written in the usual three-dimensional case as a function of the density of state effective mass in the valence band (m_v^*) as

$$N_v=4.83\times10^{15}T^{3/2}(m_v^*/m_0)^{3/2}\ \mathrm{cm}^{-3},$$

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TABLE II. Summary of the impurity concentration values and ionization energies of Sn-doped GaSe obtained from the temperature dependence of the hole concentration and hole mobility.

[Sn] (at. %)	N_{a1} (cm^{-3}) 310 meV	N_{a2} (cm^{-3}) 155 meV	N_{a3} (cm^{-3}) 70 meV	N_{a4} (cm^{-3}) $\sim$0 meV	N_d (cm^{-3})	N_{pi} (cm^{-3})
0.05	2.6×10^{17}	2.6×10^{17}			2.48×10^{17}	
0.1	6.3×10^{17}	6.3×10^{17}			5.8×10^{17}	5.4×10^{17}
0.2	2.7×10^{16}	2.7×10^{16}	1.7×10^{15}	4.07×10^{15}	4.0×10^{15}	
0.5	5.5×10^{16}	5.5×10^{16}			2.5×10^{16}	

where m_0 is the free electron mass. A first fitting of Eq. (2) to the measured hole concentrations shows that the temperature dependence of the hole concentration in samples doped with $[Sn]=0.05\%$ and 0.1% can be accounted for by considering two acceptor levels with ionization energy values of $E_a=310$ and 155 meV and with the same impurity concentration, which suggests that at low doping concentration Sn creates double acceptor centers in GaSe. At this point, we should remark that despite the fact that the statistical treatment of these double acceptors is formally different from that of two independent acceptors,[34] they can be regarded in this case as in the latter assumption, by considering that the degeneracy factor is $\beta_2=0.5$ for the shallower level and $\beta_1=2$ for the deeper one, since the difference between the ionization energies of both impurity levels is five times k_BT even at 500 K. Under these considerations, we have fitted Eq. (2) to the measured hole concentrations taking $m_v^*=0.5\ m_0$.[22] We have obtained a good agreement with experimental results (solid and dotted lines in Fig. 2). The fitting parameters are shown in Table II. The fact that compensating donors are present in all samples and that in those with the highest Sn content the hole concentration is relatively low indicates that Sn, as expected, also introduces donor centers in GaSe. Finally, in samples doped with $[Sn]=0.2\%$ the hole concentration at low temperature can be accounted for only by assuming the existence of shallow acceptor impurities with relatively low ionization energy.

Let us now discuss the possible origin of those impurity levels. It seems reasonable to assume that the donor configuration of Sn in GaSe is a substitutional position at cation site [Fig. 4(a)]. The fact that, opposite to what happens in InSe,[30–32] this center does not behave as a shallow donor in GaSe can be explained through the different structure of the conduction band of both materials. In InSe, the conduction band minimum is at the Z point and has low effective mass.[35] Impurity levels related to this minimum are shallow donors. At the L point there exist three equivalent minima with high effective mass located some 300 meV above the absolute one.[35,36] Impurity levels related to these minima are deep donors, but, being resonant at ambient pressure, they do not affect the transport properties of InSe. Under pressure the L point minima shift to lower energy and their related impurity levels enter the band gap, and trap electrons as they approach the Fermi level.[37] The structure of the GaSe conduction band at ambient pressure is similar to that of InSe under pressure. The absolute minimum at the Γ point, with low effective mass, is only a few meV below the equivalent minima at the M point, with much higher effective mass.[38] The donor level related to the Γ point minimum is shallow, with an ionization energy close to that of the exciton,[3] but the donor levels related to the M point minima are deep, trapping electrons and preventing the observation of shallow donors in GaSe by transport measurements. This model would explain why all attempts to get low resistivity n-GaSe have been unsuccessful.

With regard to the acceptor impurity configuration of Sn in GaSe, it must be pointed out that other group IV impurities, like lead (Pb), have already been shown to behave mainly as acceptors in InSe.[39] In that case, the proposed model was a Pb atom substituting for two In atoms, which would be a double acceptor, with a local configuration similar to PbI_2 or $SnSe_2$ [Fig. 4(b)].[40,41] In fact, in these compound anions are in octahedral configuration around the cation. This suggests another model as there exists in GaSe an interlayer site at which Se atoms are also in octahedral configuration [Fig. 4(c)]. It is worth noting that in both compounds the edge of this octahedron corresponds to the a parameter of the hexagonal unit cell and their values are very

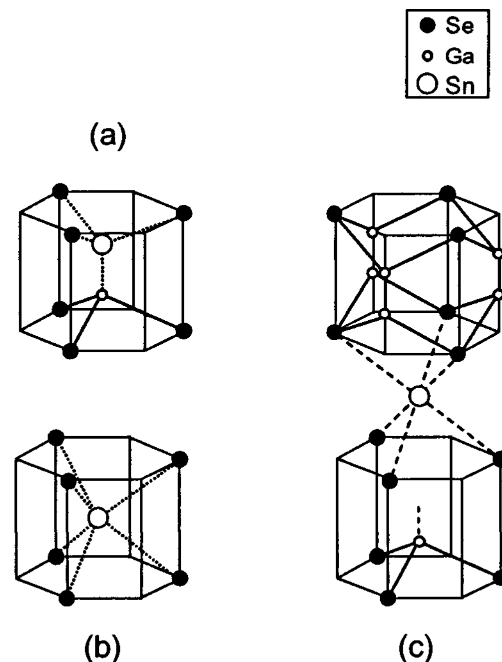

FIG. 4. (a) Proposed configuration of Sn acting as donor impurity in GaSe. In this configuration Sn substitutes for one cation. (b) Atomic configuration of Sn in GaSe in which it substitutes for two cations. In this configuration this impurity would act as a double acceptor. (c) Schematic view of the proposed configuration of Sn acting as a double acceptor in GaSe. The Sn atom is in an interlayer octahedral site bound to a close Ga vacancy.

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close to each other (3.810 and 3.755 Å in $SnSe_2$ and GaSe, respectively).[40] As the Sn–Se covalent bond length (2.57 Å) is 6% longer than the Ga–Se covalent bond (2.42 Å) the substitutional configuration can become unstable with respect to the interstitial configuration in the interlayer octahedral site, associated to a close Ga vacancy [Fig. 4(c)]. The electronic configuration of Sn in $SnSe_2$ is sp^3d^2.[40] This configuration, in the GaSe structure, would require an increase of the electron density in the interlayer space. On the other hand, this interstitial Sn atom is associated with a Ga vacancy that has acceptor character. The whole center can likely behave as a multiple acceptor.

As compensation rates are high even at low Sn nominal concentration (Table II) the substitutional Sn donor also seems to be a stable configuration. In a first stage of compensation a pairing effect can appear in which a donor center is associated with a double acceptor. The electron from the donor would be transferred to the acceptor and the electrostatic repulsion between the ionized donor and the other remaining hole would make this state become shallow. In a second stage of compensation, at very heavy Sn doping concentration, the electrons from donors occupy most of the acceptor states, mainly those at lower energy in the band gap, which have lower ionization energy. Then, holes can be generated only by excitation from the deeper states of isolated acceptors.

The temperature dependence of the hole mobility follows the trends of previously reported results.[9,22,23,29] We have calculated the hole mobility through an iteration method[42,43] by taking into account different scattering mechanisms:

(i) Scattering by 31.5 meV LO polar phonon[44] with the scattering rates given in Ref. 43. In a previous work we considered the Fröhlich constant to be that corresponding to the interaction of holes with LO polar phonons propagating along the layer planes.[22] This hypothesis has turned out to be incompatible with the pressure dependence of the hole mobility that has been recently investigated.[45] In fact, the Fröhlich constant is strongly anisotropical, as the ionicity of the material along the c axis is much lower than that along the layers. Because of the large increase under pressure of the static dielectric constant along the c axis in layered materials,[37,45] the overall ionicity also increases and the pressure dependence of the effective Fröhlich constant cannot be identified to that perpendicular to the c axis. An effective Fröhlich constant[46]

$$\alpha_h=\frac{2\alpha_{h\perp}+\alpha_{h\parallel}}{3} \tag{3}$$

has to be introduced in order to give an account of the pressure dependence of the hole mobility, where $\alpha_{h\parallel}$ and $\alpha_{h\perp}$ are the Fröhlich constant parallel and perpendicular to the c axis, respectively. From data found in the literature we have obtained values of $\alpha_{h\perp}=0.741$ and $\alpha_{h\parallel}=0.111$,[47] yielding $\alpha_h=0.531$.

(ii) Scattering by 16.7 meV A_1' homopolar optical phonon[48] through the Fivaz–Schmid relaxation time.[23,48] The hole-phonon coupling constant (g^2) was obtained by fitting the temperature dependence of the hole mobility at high temperature taking into account the above obtained value of α_h through Eq. (3), yielding a value of $g^2=0.161$.

(iii) Scattering by ionized impurities through the Brooks–Herring relaxation time[49] in which the effective ionized impurity concentration (N_I^{eff}) has been assumed to be that calculated from the temperature dependence of the hole concentration (Table II) as summation over the different ionized impurities (N_I) with a charge z as

$$N_I^{\text{eff}}=\sum_i (z^2N_I)_i=N_d+(N_{a2}^- - N_{a1}^{-2})+4N_{a1}^{-2}, \tag{4}$$

where $(N_{a2}^- - N_{a1}^{-2})$ and N_{a1}^{-2} stand for the concentration of singly and doubly ionized acceptors, respectively.

(iv) Scattering by neutral impurities through the Erginsoy relaxation time[50] in which the neutral impurity concentration (N_n) has been assumed to be that obtained from

$$N_n=N_{a2}-N_{a2}^-. \tag{5}$$

For homopolar phonon, neutral, and ionized impurity scattering mechanisms a relaxation time can be defined. It is introduced in the elastic term of the scattering rates in the iteration method. The curves obtained in this fitting process reproduce the temperature dependence of hole mobility for samples with the lowest Sn content (curve $C1$) and also for heavier doped samples in the temperature range in which holes are mainly scattered by phonons (curves $C2$, $C3$, and $C4$), but these results do not explain the anomalous behavior of the hole mobility in the temperature range in which impurity scattering dominates. This is specially true for samples doped with [Sn]=0.5%, in which the hole mobility decreases with temperature very abruptly (Table I).

As the Sn doping concentration increases a higher value of the maximum hole mobility is observed (Table I). This effect is similar to that observed early in undoped ZnSe[51] and in n-type CdS and CdTe.[52] This fact was explained by a pairing effect of donor and acceptor impurities that reduces the effective concentration of ionized impurities due to the formation of impurity complexes with a lower scattering cross section. This effect would explain the fact that the maximum hole mobility in samples doped with [Sn] =0.1% turns out to be three times higher than the calculated one (Fig. 3). In this case, the effective ionized impurity concentration must be reduced in a quantity $2N_{\text{pi}}$ (Table II) in order to reproduce its temperature dependence of the hole mobility (curve $C2'$).

Attempts to obtain an expression for the relaxation time for impurity complex scattering mechanisms have been carried out for those as dipoles[53,54] and for simple exponentially correlated impurities.[55,56] An increase of carrier mobility with increasing impurity content due to a pairing effect of impurities was predicted in both models. Nevertheless, carrier mobility increases with temperature as $T^{1/2}$ in the former and as $T^{3/2}$ in the latter. In both cases the exponents are much lower than those observed in our results (Table I). In samples

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doped with [Sn] = 0.5% the hole mobility seems to exhibit an activated behavior with an activation energy value of 50 meV in the low temperature range. In fact, at the lowest temperature, the mean free path of holes would be of the order of 0.2 Å, which means that holes are very localized and that perturbation calculations of relaxation time fail. Therefore, a hopping mechanism would better describe the hole transport process in these samples at low temperature.

V. CONCLUSIONS

Resistivity and HE measurements on Sn-doped GaSe single crystals have been carried out. All the samples appeared to be highly compensated p-type with lower resistivity than those reported in the literature for Sn-doped GaSe. The temperature dependence of carrier concentration shows that Sn can act as both acceptor and donor impurity in GaSe. Tin is proposed to introduce a double acceptor level with ionization energies of $E_a = 310$ and 155 meV. The suggested configuration for this double acceptor is a Sn atom in the interlayer octahedral site bound to a close Ga vacancy. The donor configuration can be a single substitutional Sn atom in Ga site. In a first stage close single donor double acceptor pairs give rise to centers in which the repulsion energy of the ionized donor lowers the ionization energy of the remaining hole, making this center behave as a shallow acceptor with ionization energies lower than $E_a = 70$ meV. At higher doping rates most acceptor levels are compensated and the resistivity increases.

The temperature dependence of the hole mobility has been explained by phonon and impurity scattering mechanisms. The pairing effect of impurities produces Sn-related impurity complexes with a lower scattering cross section than that for single ones. As a consequence, high quality GaSe crystals with high hole mobility and low resistivity are obtained in spite of the high doping rate.

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