Investigation of conduction band structure, electron scattering mechanisms and phase transitions in indium selenide by means of transport measurements under pressure

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Abstract
In this work we report on Hall effect, resistivity and thermopower measurements in n-type indium selenide at room temperature under either hydrostatic and quasi-hydrostatic pressure. Up to 40 kbar (= 4 GPa), the decrease of carrier concentration as the pressure increases is explained through the existence of a subsidiary minimum in the conduction band. This minimum shifts towards lower energies under pressure, with a pressure coefficient of about -105 meV/GPa, and its related impurity level traps electrons as it reaches the band gap and approaches the Fermi level. The pressure value at which the electron trapping starts is shown to depend on the electron concentration at ambient pressure and the dimensionality of the electron gas. At low pressures the electron mobility increases under pressure for both 3D and 2D electrons, the increase rate being higher for 2D electrons, which is shown to be coherent with previous scattering mechanisms models. The phase transition from the semiconductor layered phase to the metallic sodium chloride phase is observed as a drop in resistivity around 105 kbar, but above 40 kbar a sharp nonreversible increase of the carrier concentration is observed, which is attributed to the formation of donor defects as precursors of the phase transition.

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1 Introduction

Optical properties, lattice dynamics and structural phase transitions of layered III-VI semiconductors under compression have been widely investigated. Pressure experiments have shown to be an idoneous tool to investigate the specificity of chemical bonds and the electronic structure in these semiconductors. A large variety of interesting properties and behaviours have been so detected: large anisotropy and nonlinearity in the elastic properties[1, 2, 3], nonlinearity in the pressure dependence of phonon frequencies[3, 4, 5, 7] and electronic transitions[2, 5, 6, 8, 9, 10], layered phase instabilities[3, 4, 11], etc.

Unlike optical and lattice dynamical properties, transport properties of III-VI semiconductors under pressure have been little investigated. Ismailov et al[12] have reported on Hall effect (HE) and resistivity measurements in n-type indium selenide (InSe) up to 10 kbar. These authors directly relate the pressure dependence of the carrier concentration to the pressure coefficient of the direct band gap. Such a direct correlation can hardly be expected in samples exhibiting a clearly extrinsic behaviour.

In the present paper, we report on a systematic study of transport properties under high pressure, at room temperature (RT), in the layered III-VI semiconductor indium selenide doped with different donor impurities. Experimental methods are described in Section II. Results on HE, resistivity and thermopower experiments under pressure are detailed in Section III. Section IV is devoted to the discussion of results and its implications concerning the conduction band structure, electron scattering mechanisms and layered phase stability in InSe. The pressure dependence of the transport parameters below 40 kbar is consistent with a previous model in which both two-dimensional (2D) and three-dimensional (3D) electrons are considered[13].

2 Experimental

The InSe crystals were prepared by the Bridgman method from a non-stoichiometric melt $\text{In}_{1.05}\text{Se}_{0.95}$[14]. The tin (Sn) or silicon (Si) impurities were introduced in the preparation of the polycrystalline melt as selenium compounds[14, 15]. It has been shown[15] that only a small part of impurities remains in the crystal, the rest being rejected to the end of the ingot with the indium excess. Neutron transmutation doped (NTD) InSe crystals have also been analyzed in this work. The preparation, transport characterization and defect annealing of these crystals, whose Sn contents depend on the neutron dose, have been reported elsewhere[16, 17]. Samples were cleaved from the ingots with a razor blade and cut into parallelepipeds; the thickness and shape of the samples were different for each kind of experiment. All the measurements were performed at RT.
2.1 Resistivity and Hall effect measurements in hydrostatic pressure up to 12 kbar

Samples for these measurements were 10 to 30 µm thick and about 3×3 mm² in size. Contacts were made in the Van der Pauw configuration by soldering with high-purity indium. Resistivity measurements under pressure were carried out in a conventional maraging steel vessel, with pentane as pressure transmitting fluid. Moreover, HE and resistivity measurements were performed in a Unipress copper-berillium cell with the 4:1 methanol-ethanol mixture as pressure transmitting fluid. Pressure was measured in both cases with a manganine gauge.

2.2 Resistivity measurements in quasi-hydrostatic pressure up to 110 kbar

Samples for these measurements were parallelepipeds 50 to 70 µm thick and about 2×2 mm² in size. Indium contacts were made in the Van der Pauw configuration by vacuum evaporation. The pressure cell was a large volume V2 cell with a pair of tungsten carbide Bridgman anvils of 10 mm in diameter, with steel binding rings. The Bridgman gasket assembly and geometry are shown in the inset of Figure 3. Gaskets were made of pyrophyllite, the pressure transmitting medium was sodium chloride or silver chloride and the electric leads between both gasket were made of copper foil 20 to 30 µm thick. Pressure was previously calibrated with the phase transition points of a bismuth gauge.

2.3 Resistivity and Hall effect measurements under quasi-hydrostatic pressure up to 55 kbar

Samples for these measurements were parallelepipeds 50 to 70 µm thick and about 5×5 mm² in size. Ohmic contacts were made in the Van der Pauw configuration by soldering silver wires to the high-purity indium contacts pads previously vacuum evaporated. In order to obtain good contacts the end of the silver leads was previously flattened. In this case, the pressure cell consist in a pair of Bridgman tungsten carbide anvils, 27 mm in diameter, without steel binding rings. Besides the gasket thickness and diameter, and the pressure medium, which was either sodium chloride or boron nitride charged epoxy, the geometry was similar to that of the previous method.

The initial thickness of the pyrophyllite gaskets was 0.5 mm and the diameter of the hole was 9 mm. They were treated at 680°C during one hour for getting suitable mechanical properties and avoiding the break of the gaskets in the first stages of the compression. Before the prefiring, four channels were made in one of the gasket to place the silver wires. Bridgman anvils were put between the pistons of a 300 tonnes press. The pressure was determined by calibration of the oil pressure against the bismuth
phase transition points. A copper coil was placed around one of the pistons. The
magnetic field intensity in the gap between the anvils was measured by means of a Hall
effect probe, as a function of the distance between them, and was 0.6 T at the normal
working distance (0.8 mm).

2.4 Thermopower

Thermopower measurements under pressure were carried out in the system
described in subsection 2.2. The geometry of the gasket and sample assembly is shown
in the inset of Figure 6. One point of the sample is heated by Joule effect in a thin
constantan strip in thermal contact with it and soldered to Cu leadtrhoughs. In high
pressure conditions a stationary thermal gradient is quickly attained due to the thermal
conduction through the anvil-gasket assembly. Two strip Cu/Constantan thermocou-
lples are used to measure both the temperature gradient and the Seebeck voltage in the
sample.

3 Results

3.1 Resistivity measurements in hydrostatic pressure

Figure 1 shows the resistivity ($\rho$) as a function of pressure for several InSe samples.
Five of them (curves 1 to 5) were chosen as representative for well characterized three-
dimensional behaviour in their transport properties[16, 13, 21]. For concentrations
lower than $10^{16}$ cm$^{-3}$ a slight decrease of the resistivity is observed between ambient
pressure and 8 kbar followed by a slight increase up to 12 kbar (sample 1). The rest of
those samples exhibit a regular trend: the resistivity increase under pressure is more
pronounced for higher electron concentrations ($n$). On the other side, samples with
well characterized two-dimensional behaviour in their transport properties[21] exhibit
a resistivity decrease under pressure (curves 6 and 7).

3.2 Hall effect under hydrostatic pressure

Figures 2-a and 2-b show the electron concentration and mobility ($\mu$), respectively
as a function of pressure up to 12 kbar for Si-doped, Sn-doped and NTD InSe samples.
Within this range of pressure the electron mobility monotonically increases with pres-
sure in all of them. The resistivity increase under compression in the Sn-doped and
NTD samples is then mainly due to the decrease of the carrier concentration. In the
other side, in Si-doped samples the electron concentration slightly increases with pres-
sure. Thus, the increase of both the mobility and the carrier concentration produces the
observed decrease of the resistivity (Figure 1). It must be outlined that the apparent
electron concentration at zero pressure is very similar in one of the Sn-doped samples
(○) and one of the Si-doped samples (△). Nevertheless, their transport properties (\(\rho\), \(n\) and \(\mu\)) have a completely different behaviour under compression. Then, pressure effects in the transport properties of InSe turn out to be very sensible to the dimensionality of charge transport, which was established through independent experiments (resistivity anisotropy, photo Hall effect, etc.)[13].

### 3.3 Resistivity measurements under quasi-hydrostatic pressure up to 110 kbar

Figure 3 shows the resistivity as a function of pressure for a Sn-doped and a Si-doped InSe sample, with an effective electron concentration of \(10^{17}\) cm\(^{-3}\) and \(6 \times 10^{16}\) cm\(^{-3}\) at ambient pressure, respectively. It can be seen there that, above 10 kbar in the Sn-doped sample and above 20 kbar in the Si doped one, the resistivity exponentially increases up to around 40 kbar. It reaches a maximum centered at about 45 kbar and then monotonically decreases up to 100 kbar. An abrupt decrease is also observed at around 105 kbar. It must be outlined that changes over the resistivity maximum are not reversible. Points of curve 2 were taken for decreasing pressures.

### 3.4 Hall effect and resistivity measurements under quasi-hydrostatic pressure

Figures 4 and 5 show the resistivity, the electron concentration, and Hall mobility as a function of pressure for different InSe samples doped with Sn and Si, respectively. In the range of pressure up to around 12 kbar, these results confirm those of Figures 1 and 2. Having the electron concentration a weak pressure dependence up to 25 kbar in Si-doped samples, the resistivity decrease turns out to be a direct consequence of the electron mobility increase under compression. Above that pressure, both the carrier concentration and the mobility have a slow decreasing behaviour providing an increase of the resistivity. On the contrary, above 12 kbar in the Sn-doped samples the electron concentration decreases by one order of magnitude and the mobility by factor 3 to 5. In addition, from Figure 4 it is clear again that in samples with 3D behaviour the increase rate of the resistivity is stronger for those with higher electron concentrations at zero pressure. Notice that, in one of the Sn-doped samples (○) the pressure range could be extended up to 55 kbar, i.e. above the resistivity maximum of Figure 3. The resistivity decrease above 45 kbar appears to be associated to a sharp increase of the electron concentration.

### 3.5 Thermopower measurements under quasi-hydrostatic pressure

Figure 6 shows the thermopower as a function of pressure for a Sn-doped InSe
sample. The thermopower decreases with lowering pressure in all the measured range and this decrease is sharper in the pressure range around 40-50 kbar. At the highest pressure, the thermopower value (about 10 mV/K) is typical of a degenerate semiconductor, coherently with the low value of resistivity observed in this pressure range (Figure 3).

4 Discussion

4.1 Conduction band structure

Hall effect results in InSe samples with well characterized 3D behaviour show that the electron concentration decreases as pressure increases up to some 40 kbar. This behaviour cannot be attributed to the pressure change of the band gap (the electron concentration remains in the extrinsic range) and neither to the change of the ionization energy of the tin related shallow donor, which is fully ionized at RT. At ambient pressure this ionization energy is 17.4 meV\[22\], which is very close to the ideal hydrogenic donor in InSe. The hole effective mass being very high in InSe, the pressure change of the shallow donor ionization energy should be very similar to that of the exciton binding energy, that has been shown to decrease under compression\[10\]. That effect, also observed in GaSe\[2\], was attributed to the increase of the static dielectric constant under pressure. This hypothesis has been verified in the related compound GaS\[23\] and recently in GaSe\[24\].

The decrease of the electron concentration under pressure has been observed in III-V semiconductors and explained through the existence of subsidiary minima in the conduction band moving to lower energies with respect to the absolute minimum (L and X minima with respect to the \( \Gamma \) minimum in GaAs). According to band structure calculations\[25, 26\] there exist subsidiary minima in the conduction band of InSe located a few hundreds meV above the absolute one. In the related compounds GaS and GaSe these minima are responsible for the indirect absorption edge, whose pressure coefficient are of the order of some -100 meV/GPa\[2, 8\]. In the case of InSe, the pressure behaviour of the exciton peak, which broadens and disappears above 25 kbar, has been explained through the interaction with an excited minimum of the conduction band, moving to lower energies under pressure\[10\]. The decrease of the electron concentration under compression is coherent with the assumption that, related to the excited minimum, there exist a localized level resonant with the conduction band at ambient pressure. As this excited minimum moves to lower energies with the pressure increase, the related impurity level reaches the forbidden band before the semiconductor becomes indirect. Then it traps electrons as it approaches the Fermi level \( E_F \). If we assume that all hydrogenic levels are ionized and the 3D electron concentration \( n_3 \) decrease is due to trapping, the free electron concentration and the trapped electron concentration \( n_T \) as a function of pressure \( P \) are given by:
\[ n_3(P) = N_C(P)e^{-\frac{E_C(P) - E_F(P)}{K_B T}} \quad (1) \]

and

\[ n_T(P) = n_3(0) - n_3(P) = N_D - n_3(P) = \frac{N_T}{1 + \frac{1}{2}e^{-\frac{E_T(P) - E_F(P)}{K_B T}}} \quad , \quad (2) \]

where \( N_D \) is the shallow donor concentration, \( N_T \) is the deep impurity level concentration, \( T \) is the absolute temperature, \( K_B \) is the Boltzman constant, and \( E_C \), \( E_F \) and \( E_T \) are the conduction band absolute minimum, the Fermi level, and the excited minimum related impurity level energies, respectively. If we assume that all impurity levels are associated to the tin impurities, we can make \( N_T = N_D \) and, neglecting the pressure change in the effective density of states \( N_C \), we can obtain, from Equations (1) and (2), the pressure dependence of \( E_F \) and \( E_T \) with regards to the absolute minimum of the conduction band. Figure 7 shows the results of this model. A least square fit to \( E_T - E_C \) data with a quadratic function (dashed line in Fig. 7) gives:

\[ E_T - E_C = 100(15) - 10.5(2)P(\text{meV/kbar}) + 0.04(0.02)P^2(\text{meV/kbar}^2) \quad , \quad (3) \]

where \( P \) is in kbar. Thus, at ambient pressure and temperature the deep level lies at some 100 meV above the absolute minimum of the conduction band. Furthermore, the pressure coefficient of the excited minimum impurity level turns out to be -105 meV/GPa, i.e. very close to the pressure coefficients of indirect absorption edge in GaS and GaSe.

### 4.2 2D electrons

The presence of 2D electrons in InSe and the role that they play in transport properties has been widely investigated \[27]-[32]. The origin of 2D electrons in InSe is extrinsic. The 2D states are electric subbands that have been attributed to quantum size effects in thin layers limited by stacking fault related barriers[13]. Other authors have proposed a model in which 2D electronic subbands in InSe are created by a high concentration of donor impurities bound to a stacking fault, like in \( \delta \)-doping systems[32]. This model is inconsistent with the low areal concentration and high 2D electron mobility in InSe at low temperature. Below 20 K, transport properties are dominated by 2D electrons in most n-type InSe samples. At RT, among samples with effective electron concentrations of the order of \( 10^{17} \text{ cm}^{-3} \), only Si-doped InSe exhibits 2D behaviour, which can been attributed to the lower solubility of Si in InSe with
respect to Sn, which makes a part of Si atoms to deposit in interlayer positions bound
to the stacking fault, so increasing the 2D electron concentration.

It is to be outlined that transport measurements under pressure give a suplementary
evidence of the specificity of Si-doped samples. This behaviour can be interpreted in the
framework of the subband model proposed in Reference [13]. Between planar defects,
to which 2D electrons are associated, the 3D electron concentration in Si doped InSe
remains relatively low: from far infrared absorption[22], the concentration of Si-related
shallow donor was estimated to be of the order of $5 - 6 \times 10^{15}$ cm$^{-3}$. It means that the
Fermi level at RT is some 120 meV below the conduction band. Then, these samples
behave as 3D samples with a low electron concentration. The deep center related to
the excited minimum in the conduction band does not trap 3D electrons because the
Fermi level is deep in the forbidden band. On the other hand, electron in the electric
2D subbands are degenerate; owing to this characteristic, most of them occupy energy
states below the Fermi level. In this way, 2D electrons are not trapped until the deep
level crosses the Fermi level, which occurs at much higher pressures. If we assume that
the change of resistivity is mainly due to the decrease of the 2D electron concentration
($n_2$) due to trapping, we can also try to estimate the pressure coefficient of the trap with
respect to the bottom of the 2D electric subband ($E_{C2}$). The electron concentration is
related to the Fermi level through the well known equation[33]:

$$n_2(P) = \frac{m^*K_B T}{\pi\hbar^2} \ln \left(1 + e^{\frac{E_F(P) - E_{C2}(P)}{K_B T}}\right). \tag{4}$$

On the other side, 2D electrons in InSe are extrinsic. They are provided by donor
centers located between stacking faults. Their energy level related to the absolute
minimum is shallow and is affected by quantum confinement effects, that are the origin
of the 2D subbands according to the model proposed in Ref. [13]. On the opposite,
their level related to the second minimum would be deep and localized and then it is
not affected by the quantum confinement effects, behaving then as electron trap as it
crosses the Fermi level under pressure. We can consider, like in the previous subsection,
that the trap concentration is the total number of 2D electrons at ambient pressure.
Then, the concentration of trapped electrons in each 2D defect ($n_{T2D}$) will be given by:

$$n_{T2D} = n_2(0) - n_2(P) = \frac{n_2(0)}{1 + \frac{1}{2} e^{\frac{E_F(P) - E_{C2}(P)}{K_B T}}} \tag{5}$$

From Equations (4) and (5) we can obtain the pressure change of the trap level
with respect to the bottom of the subband, that is shown in Figure 7. The pressure
coefficient turns out to be -110 meV/GPa, of the same order that the one obtained
from results in samples with 3D behaviour.
4.3 Electron scattering mechanisms

The pressure dependence of the electron Hall mobility provides us with a supplementary test of electron scattering mechanisms in InSe. As regards 3D electrons in the absolute minimum of the conduction band, the electron mobility ($\mu_3$) in InSe at room temperature has been shown to be controlled by both polar and homopolar phonon scattering and by ionized impurity scattering mechanisms \cite{13}. For scattering by polar phonons an iterative method must be used \cite{34}. The Schmid-Fivaz relaxation time \cite{35} for homopolar phonon scattering and the Brooks-Herring relaxation time \cite{36} for ionized impurity scattering can be introduced in the elastic term of the scattering rates in the iterative method.

The scattering rates of 3D electrons depend on the phonon energies, through the phonon occupation number ($N$), and on the corresponding electron phonon coupling constant. In the case of homopolar optical phonon scattering, the electron phonon coupling constant is:

$$g^2 = \frac{D_0^2 m_3^*}{2\sqrt{2\pi} N \hbar(\hbar\omega_{hp})^{3/2}}$$

(6)

where $D_0$ is the deformation potential and $m_3^* = (m_\perp^* m_\parallel^*)^{1/2}$, being $m_\perp^*$ and $m_\parallel^*$ the electron effective mass perpendicular and parallel to the $c$-axis, respectively. The value at atmospheric pressure of this coupling constant is $g^2=0.028$ \cite{13} and the phonon involved is the $A'_1$ homopolar optical mode with wavelength: $\omega_{hp} = 115 \text{ cm}^{-1}$ \cite{37}.

In the case of polar phonon scattering mechanism, the coupling constant is the Fröhlich constant, that is given by:

$$\alpha = \frac{e^2 \sqrt{m^*}}{\sqrt{2} \hbar \sqrt{\hbar \omega_{LO}} \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right)}$$

(7)

where $e$ is the electron charge and $\epsilon_\infty$ and $\epsilon_0$ stand for the high-frequency and static dielectric constants. As the electron scattering rates for LO phonons are obtained through an integration over all the possible directions of the phonon momentum, this constant has to be averaged over the whole solid angle. Assuming that its main angular dependence arises from the variation of the dielectric constant \cite{38}, its value at room pressure is $\tilde{\alpha} = 0.144$ \cite{13}. The wavelength of the LO phonon is: $\omega_{LO} = 211 \text{ cm}^{-1}$ \cite{37}.

The pressure dependence of the quantities involved in Equations (6) and (7) are reasonably well known. The effective masses at atmospheric pressure can be taken from Reference \cite{28}, $m_\perp^* = 0.141m_o$ and $m_\parallel^* = 0.081m_o$ being $m_o$ the free electron mass. In the framework of the $k.p$ theory \cite{33} their variation with pressure is proportional to the direct band gap ($E_g$) variation. The perpendicular component of static dielectric constant $\epsilon_{0\perp}$ is nearly constant \cite{5} and the variation of $\epsilon_{0\parallel}$ can be obtained from the
behaviour under pressure of the exciton binding energy ($R$)\[10\]. Thus, the decrease of $R$ imposes that $\varepsilon_{0||}$ increases strongly from 7.8 to 10.9 up to about 40 kbar. This behaviour has been also observed in related compounds\[2, 23, 24\] and it was explained through the charge transfer from intralayer to interlayer space\[2\]. Finally, the pressure dependence of $\varepsilon_{\infty||}$ and $\varepsilon_{\infty\perp}$ can be calculated from that of $\varepsilon_0$ and the phonon frequencies.

Table I gives the atmospheric pressure value assumed for the dielectric constant\[40, 41\], the pressure coefficient of the phonons\[7\] and the reference from which they were taken. Once the behaviour under pressure of all the parameters is known, we can calculate the mobility for 3D electrons ($\mu_3$) by considering different compensation ratio ($x$). Figure 8 shows the results of this calculation.

As regards the 2D electron, according to the model proposed in Reference \[13\], the electron mobility determined by homopolar optical phonon scattering is much smaller than the 3D electron mobility due to the higher value of the effective electron-phonon coupling constant ($g_{\varepsilon_f}^2$), that depends on the localization parameter of 2D electrons along the c-axis ($b_0$):

$$g_{\varepsilon_f}^2 = \frac{3\pi}{8} \sqrt{\frac{\hbar^2 b_0^2}{2m^*_\perp^2 \hbar \omega_p}} g^2,$$

where

$$b_0 = \sqrt{\frac{33e^2 m^*_\parallel n_s}{8\varepsilon_{0||} \hbar^2}}$$

and where $n_s$ is the density of 2D electron per unit area in the planar defects. As we pointed out above, the pressure dependence of the involved quantities are well known and can be taken from literature. The mobility for the 2D electrons ($\mu_2$) can be calculated in the relaxation time approximation and the results are also shown in Figure 8. The higher relative increase of 2D electron mobility with respect to that of 3D electrons is mainly due to the decrease of the localization parameter $b_0$, as $\varepsilon_{0||}$ increases under pressure.

It is to be outlined that the model proposed in Reference \[13\] to explain the temperature dependence of electron mobility in a large variety of InSe samples can also explain the pressure effects. In the framework of this model, once computed separately the pressure dependence of the 2D mobility ($\mu_2$) and 3D mobility ($\mu_3$), we have calculated the pressure dependence of the Hall mobility and the apparent electron concentration by means of\[12\]:

$$\mu = \frac{n_2\mu_2^2 + n_3\mu_3^2}{n_2\mu_2 + n_3\mu_3}$$
and

\[ n = \frac{(n_2 \mu_2 + n_3 \mu_3)^2}{n_2 \mu_2^2 + n_3 \mu_3^2}. \]  

(11)

Taking \( n_2, n_3 \) and \( x \) at room pressure as fitting parameters, we fit Equations (10) and (11) to the experimental results. Fits are shown in Figure 9 and the agreement with the experimental results is quite good. In the Sn-doped samples the decrement of \( n_3 \) under pressure, due to the presence of the trapping centers, makes that \( n_3 \) becomes smaller than \( n_2 \) at around 20 kbar. As 2D electrons have a smaller mobility than the 3D ones (see Fig. 8), the decrease of \( n_3 \) is then responsible for the drop of the Hall mobility. Instead of that, in Si-doped samples such a strong decrease of the mobility is not observed because \( n_2 \) is of the same order that \( n_3 \). In this way, the behaviour of the effective electron concentration and the mobility are less sensitive to the decrease of \( n_3 \). In fact, the slight increase of the carrier concentration observed in some samples can be also accounted for. If \( n_2 \geq n_3 \), at ambient pressure, \( n \) is closer to \( n_3 \) due to the higher mobility of the 3D electrons. As \( n_3 \) decreases under compression, \( n \) tends to \( n_2 \) and then slightly increases.

### 4.4 Phase transition and precursor effects

Resistivity measurements at high pressure can give information about the transition from the layered structure to the NaCl-type metallic phase, that was detected at about 100 kbar through x-ray diffraction and reflectivity measurements[3]. In Figure 3 a resistivity drop is observed that can be related to this semiconductor-metal transition. Nevertheless, resistivity measurements show that some irreversible changes occur in the material at much lower pressures. The resistivity decrease starting at about 45 kbar corresponds to the thermopower drop that is also observed above that pressure. Both process are nonreversible and suggest that there is a pressure above which some kind of structural instability occurs, leading to the creation of a large concentration of donor centers that make the material to show a degenerate behaviour. Other authors have observed that above 60 kbar the sample becomes irreversibly opaque[7, 10]. From reflectivity measurements[3], it has been also shown that a plasma reflection structure is observed at 80 kbar, i.e., 20 kbar below the transition to the metallic phase. If we assume that the reflectivity minimum, that occurs at \( \omega_s = 0.8 \) eV, corresponds to the plasma frequency, then the electron concentration (for an effective mass of the order of \( m_e \)) would be of the order of \( 10^{21} \) cm\(^{-3}\). Results of Figure 4 (c) show that the resistivity decrease is due to the sharp increase of the electron concentration. The highest measured electron concentration is of the order of \( 10^{18} \) cm\(^{-3}\). As the resistivity still lowers by three orders of magnitude, the electron concentration would be of the same order of that estimated from the value of the plasma frequency, which is also coherent with the low value of the thermopower.
In the metallic phase, if one assumes an electron per unit cell, the electron concentration would be of the order of $2.5 \times 10^{22} \text{ cm}^{-3}$. It means that before the transition the defect concentration is very high, of the order of 1 defect per 20 to 25 unit cells. In this range of pressure the layered phase seems to be stable only when it contains a high defect concentration. It is reasonable to conceive those defects as precursors of the phase transition. The atom plane sequence of the layer phase (Se-In-In-Se) must change to the Se-In-Se-In sequence of the NaCl-type phase. A precursor defect of the high pressure plane sequence would be one in which a In atom shifts from the intralayer position to an interlayer octahedral site, typical of the NaCl-type structure. Raman measurements under pressure show that in layered crystals from the III-VI family there is a charge transfer from the In-In intralayer bonds to the interlayer space, which increases the overall ionicity of the crystal under pressure. These results indicate that the In-In intralayer bond tends to be relatively weakened. A possible precursor defect that fills all the conditions would be that represented in Figure 10, in which an In-In bond is broken and one of the In atoms jumps to the octahedral interlayer site, giving rise to 2 dangling cation bonds. In partly ionic compounds, cation dangling bond occur in anion vacancies that have donor character. It seems then to be reasonable to attribute donor character to the defect here proposed.

5 Conclusions

Systematic Hall effect, resistivity and thermopower measurements have been carried out in Sn-doped and Si-doped and NTD InSe. The strong decrement of the electron concentration under compression in samples exhibiting a 3D behaviour is explained through the existence of an excited minimum in the conduction band, which shifts towards lower energies with a rate of -105 meV/GPa as pressure increases, and whose related impurity level traps electrons as it approaches the Fermi level. The behaviour of transport parameters under pressure up to 40 kbar in different samples has been explained through a model in which both 3D and 2D electrons has been taken into account. The fit of this model to the experimental results is quite satisfactory. In addition, around 50 kbar a sharp increase of the electron concentration was detected. Above this pressure both resistivity and thermopower changes start to be nonreversible, this is an evidence of a pressure-induced structural instability of InSe. These phenomena have been related with the presence of defects which are precursor of the phase transition to the NaCl metallic phase. This transition has been observed as a drop in the resistivity at around 105 kbar.

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Table captions

**Table I**: Dielectric constants at room pressure and pressure dependence of the phonon frequencies.
Figure captions

Figure 1: Resistivity as a function of hydrostatic pressure for several n-type InSe samples. The lines are just guides to the eye.

Figure 2: (a) Electron concentration and (b) mobility as a function of hydrostatic pressure for Sn (□ and △) and Si (○ and ◇) doped and NTD (●) InSe samples.

Figure 3: Resistivity as a function of pressure for a Sn-doped InSe sample in quasi-hydrostatic conditions. Curves 1 were taken during upstroke and curves 2 during downstroke. The inset shows the experimental assembly.

Figure 4: Resistivity, electron concentration and mobility as a function of pressure for several Sn-doped InSe samples under quasi-hydrostatic conditions.

Figure 5: Same as Fig. 4 for two Si-doped InSe samples under quasi-hydrostatic conditions.

Figure 6: Thermopower as a function of pressure for one Sn doped sample in quasi-hydrostatic conditions. The inset show the experimental assembly.

Figure 7: Change under pressure of the Fermi level ($E_F$) and the deep impurity level ($E_T$) with regards to the absolute minimum of the conduction band ($E_C$) (○, □) and to the bottom of the 2D subbands ($E_{C2}$) (●).

Figure 8: calculated $\mu_2$ (6) and $\mu_3$ (1 to 5) by assuming different concentration ratio and taking $n_3 = 8 \times 10^{16}$ cm$^{-3}$ and $n_2 = 5 \times 10^{15}$ cm$^{-3}$. (1) no compensation, (2) 20 %, (3) 40 %, (4) 60 % and (5) 80 %. The dashed line gives the result of a fit to the data points by using a second order polynomial (see Eq. (3)). The solid lines are just guides to the eye.

Figure 9: Fitting through the model proposed in section 4 to the experimental (a) Hall mobility and (b) electron concentration.

Figure 10: Schematic view of the possible precursor defect originated by the jump of an In atom from the intralayer space (a) to the interlayer space (b). (○) In atoms and (●) Se atoms.
| $\epsilon_{\infty\perp}$ | $\epsilon_{\infty\parallel}$ | $\epsilon_{0\perp}$ | $\epsilon_{0\parallel}$ | $\delta\omega_{hp}/\delta P$ (cm$^{-1}$/kbar) | $\delta\omega_{LO}/\delta P$ (cm$^{-1}$/kbar) |
|-----------------|-----------------|-----------------|-----------------|------------------|------------------|
| 7.4             | 7               | 10.9            | 7.8             | 0.54             | 0.36             |
| Reference       | 40              | 40              | 41              | 41               | 7                | 7                |
\begin{tabular}{|c|c|}
\hline
Dop. & n ($10^{16}$ cm$^{-3}$) \\
\hline
1 & Si 0.65 \\
2 & NTD 6.0 \\
3 & Sn 7.9 \\
4 & Sn 8.3 \\
5 & NTD 15.1 \\
6 & Si 10.8 \\
7 & Si 3.0 \\
\hline
\end{tabular}
InSe:Sn

ρ (Ωcm)

10
1
0.1

P (kbar)

0 10 20 30 40 50 60

n (cm⁻³)

10¹⁸
10¹⁷
10¹⁶
10¹⁵
10⁴
10³
10²
10¹
1

μ (cm²/Vs)

1000
100
10
1
THE RMOP O WE R (m V/K)

InSe:Sn

Cu leadthroughs
hot point
sample
thermocouples

THERMOPOWER (mV/K)

InSe:Sn

P (kbar)
