Transport measurements under pressure in III–IV layered semiconductors

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This paper reports on Hall effect, resistivity and thermopower effect measurements under high pressure up to 12 GPa in p-type γ-indium selenide (InSe) and ε-gallium selenide (GaSe). The paper focuses on two applications of transport measurements under pressure: electronic structure and phase transition studies. As concerns the electronic structure, we investigate the origin of the striking differences between the pressure behaviour of transport parameters in both layered compounds. While the hole concentration and mobility increase moderately and monotonously in ε-GaSe up to 10 GPa, a large increase of the hole concentration at near 0.8 GPa and a large continuous increase of the hole mobility, which doubled its ambient pressure value by 3.2 GPa, is observed in γ-InSe. Based on electronic structure calculations the difference is found to arise from the pressure evolution of the valence band maximum. While the shape of the valence band maximum is virtually pressure-insensitive in ε-GaSe, it changes dramatically in γ-InSe, with the emergence of a ring-shaped subsidiary maximum that becomes the absolute valence-band maximum as pressure increases. Transport measurements as a function of pressure and temperature are also used to investigate the phase diagram of InSe and, in particular, the transition to the rock-salt polymorph.
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This paper reports on Hall effect, resistivity and thermopower effect measurements under high pressure up to 12 GPa in p-type $\gamma$-indium selenide (InSe) and $\epsilon$-gallium selenide (GaSe). The paper focuses on two applications of transport measurements under pressure: electronic structure and phase transition studies.

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1 Introduction

Transport measurements have been widely used in high pressure research since the foundational period (1) and have been applied to semiconductor physics since the very beginning (2). Nevertheless, since the appearance of the diamond anvil cell (3), optical measurements have certainly been the technique of choice in high pressure semiconductor research (4). This has been the case for III–VI layered materials, and, in particular, in which concerns the effect of the layer stacking sequence in their electronic properties. The symmetry ($D_{3h}$) is identical for the isolated layer of three of the most studied members of this family (InSe, GaSe, GaS) but not for bulk compounds, as each layer stacking sequence leads to a different polytype, with a different crystal symmetry: $\gamma$-polytype for InSe (C$_3$, point group) [5], $\epsilon$-polytype for GaSe ($D_{3h}$, point group) [6] and $\beta$-polytype for GaS ($D_{5h}$, point group) [7]. The effect of the polytype symmetry in the lattice dynamics is obviously very clear (through the selection rules for Raman effect) and has been widely investigated [8–11]. By contrast, its effect in optical and transport properties is far less obvious. It is worth noticing that the absorption edges of $\gamma$-InSe and $\epsilon$-GaSe exhibit virtually the

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same features and intensity, apart from the photon energy shift [11–13]. In spite of the number of extrinsic parameters involved in transport properties, transport measurements under pressure can be a very efficient tool to detect changes in the band structure. In the case of InSe, the energy difference between the indirect subsidiary minima and the direct absolute minimum of the conduction band decreases upon compression, and a direct-indirect band-gap crossover occurs at 4 GPa [13, 15]. These changes of the conduction-band structure affect the transport properties of n-type InSe. Hence, research of the transport properties of n-type under compression [16, 17] valuably contributed to the understanding of the pressure behaviour of the conduction-band structure of InSe.

Density-functional-theory (DFT) electronic structure calculations showed that the valence-band structure of InSe exhibits a complex behaviour under pressure leading to a non-conventional direct-to-indirect crossover [13, 15, 18, 19]. The valence band of InSe above 4 GPa exhibits a singular feature: a ring-shaped (toroidal) constant energy surface [15]. These changes of the valence-band structure of InSe strongly affect the transport properties of p-type InSe [20], but not those of p-type GaSe [20, 21].

In this paper we intend a further investigation of these effects by extending the pressure range up to 12 GPa and including also thermopower measurements. After a brief description of the experimental method and the band structure calculations in Section 2, we will present the experimental results in Section 3 and discuss them on the basis of the evolution of the electronic structure of both compounds under pressure in Section 4.

2 Experimental details

Hall effect (HE), resistivity and thermopower measurements under pressure were performed using steel-belted Bridgman-type opposed tungsten carbide (WC) anvils with a tip of 15 mm in diameter. The sample was contained in an annealed pyrophyllite gasket with BN (h-BN) as pressure-transmitting medium. A 150 ton oil press was used to apply the load in the opposed anvils. A pressure of 13 GPa can be obtained routinely with this arrangement [21], which has been described in detail elsewhere [16, 17]. The sample pressure was determined by the calibration of the load applied to the anvils against high-pressure resistivity transitions in calibrants like Bi, Yb, CdTe and n-type InSe [21–28], being linearly extrapolated above 10.5 GPa.

The present studies were performed in InSe and GaSe monocrystals grown by the Bridgmann method [29, 30]. The samples used for the measurements were typically 30–40 µm thick and 3 × 3 mm² in size. Silver (Ag) or Gold (Au) contacts were vacuum evaporated on the corners of the samples in the van der Paw configuration [31] taking care that the contact size was always much smaller than the distance between contacts. Ag wires of 100 µm in diameter were used as electrical leads, being soldered with a silver conductive epoxy to the evaporated electrodes. To avoid inaccuracy problems in the determination of the Hall coefficient (RH) coming from offset voltages, we acquired two sets of HE measurements, one for positive and one for negative magnetic field (0.19 T) directions. The linearity of the ohmic voltages on the injected current was checked out at different pressures. HE and resistivity measurements at high temperatures and under pressure were carried out in the set-up described in Ref. [32].

For thermopower measurements under pressure, Ag or Au ohmic contacts were deposited on both ends of 1 × 4 mm² samples. Two Ag wires were used for measuring the thermo electromotive force (e.m.f.). A 25 µm thick rhenium strip, connected to two Cu wires was used as a heating element to create the temperature gradient, that was measured with two steel-shielded K-type thermocouples placed opposite to the Ag wires.

3 Results

Figures 1 and 2 show the resistivity (ρ), hole concentration (p), and hole mobility (µ) as a function of pressure for a sample of p-type GaSe and a sample of p-type InSe, respectively. The nominal doping concentration of each sample is given in the figures. The 1 bar values of ρ, p, and µ agree with values in the Ref. [30, 33]. In GaSe, ρ decreases with pressure in a monotonous way. This decrease is a conse-
sequence of the increase of $p$ and $\mu$. The hole concentration duplicates its 1 bar pressure value at 8 GPa. Beyond this pressure it bends towards the pressure axis becoming nearly constant above 10 GPa. The mobility increases a 25% from 1 bar to 8 GPa, and remains unchanged above this pressure. The behaviour of the transport parameters of InSe under compression is quite different from the behaviour observed in GaSe. In InSe $\rho$ shows a flat behaviour up to 0.8 GPa, but above this pressure an abrupt decrease of $\rho$ is observed. From 0.8 to 4.5 GPa $\rho$ falls more than one order of magnitude. This change of $\rho$ is a consequence of the abrupt increase observed in $p$ above 0.8 GPa. On the other hand $\mu$ shows a monotonic behaviour doubling its 1 bar value by 4.5 GPa. The resistivity also shows two additional features, an abrupt change of the slope at 4.5 GPa and a decrease of two orders of magnitude near 10.5 GPa. The first change is the consequence of a carrier-type inversion and the second one a characteristic of the transition to the metallic NaCl-type structure of InSe [34]. After the carrier-type inversion the electron concentration increases upon compression reaching a value close to $10^{20}$ cm$^{-3}$ at 7.5 GPa. At the same time, the Hall mobility decreases from 43 cm$^2$/Vs at 4.5 GPa to 1 cm$^2$/Vs at 7 GPa.

Figure 3 shows the thermoelectric power as a function of pressure for n- and p-type InSe and for p-type GaSe. For p-GaSe, the thermopower slightly decreases from 1 bar to 4 GPa and then remains fairly constant up to 9 GPa.

The pressure dependence of thermopower in InSe is more complex. For n-InSe, an increase is observed up to 4 GPa. Between 4 and 6 GPa the thermopower exhibits a quick drop from 600 to 30 $\mu$V/K, followed by a monotonous decrease up to 10.5 GPa. At this pressure, a further drop of one order of magnitude leads to typically metallic values around 2 $\mu$V/K.
For p-type InSe, the thermopower presents first a drop between 1 and 2 GPa and then a monotonous decrease up to 4 GPa. A quick decrease starts at 4 GPa, followed by a change of sign at 6 GPa, pressure at which the evolution becomes similar to that of n-InSe, even at the phase transition pressure.

4 Discussion

The behaviour of the transport parameters of p-type GaSe here reported confirms our previous measurements up to 4 GPa [35]. Above this pressure, we did not observe any significant change of the transport parameters. The observed increase of $p$ and $\mu$ can be quantitatively explained through a reduction of the activation energy of the acceptor levels and a decrease of the hole-phonon coupling constants [35]. This two facts are a direct consequence of the large increase upon compression of the static dielectric constant in the direction parallel to the $c$-axis [36, 37].

In p-type InSe, the present results agree very well with the previous results we reported up to 3 GPa [20]. The changes observed in $\mu$ and $p$ up to 4.5 GPa are the consequence of a change in the valence-band structure under pressure [13, 15]. The large increase of both transport parameters under pressure can be understood on the basis of a corresponding large increase of the density of states and a decrease of the effective mass in the valence-band maximum (VBM). These apparently contradictory conditions are fulfilled by the appearance under compression of a ring shaped VBM [15, 20]. By contrast to the VBM at $\Gamma$, in which the density of states has the well known dependence on the hole effective mass and energy, in the ring shaped maximum, the density of states is constant and proportional to the radius $k_{RS}$ of the circumference at which the new energy maximum occurs:

$$g_{VI}(E) = \frac{1}{2\pi} \left( \frac{2m^{*}_{he}}{\hbar} \right)^{1/2} E^{3/2},$$

$$g_{VRS}(E) = \frac{m^{*}_{he} k_{RS}}{\pi \hbar^2} = G_0,$$
where \( m_{\text{ring}}^* \) is the effective mass around the ring shaped VBM [20]. A straightforward deduction based in the relaxation time approximation of Boltzmann equation shows that the hole mobility at the ring-shaped VBM is controlled by the value of \( m_{\text{ring}}^* \), that is much smaller than \( m_{\text{Γ}}^* \), in spite of the much larger density of states (as this one is proportional to the ring radius).

DFT calculations have shown that in InSe this maximum becomes the absolute maximum above 3 GPa [13]. They also predict that no change of the VBM occurs under pressure in GaSe [20]. This is fully coherent with the monotonous change of all hole transport parameters in p-type GaSe (see Fig. 1).

As regards the pressure evolution of the thermopower, let us first point out that, in the case of GaSe the decrease from 800 to 500 \( \mu V/K \) between 1 bar and 4 GPa is consistent with the increase of the hole concentration and the slight decrease of the hole effective mass in the same pressure range, while the constancy beyond 4 GPa reflects the constancy of the hole concentration.

For n-InSe, thermopower increases up to 4 GPa, which corresponds to the decrease of the electron concentration by nearly two orders of magnitude, due to the trapping of electrons by a deep center associated to the direct to indirect crossover in the conduction band [16]. In the case of p-InSe, the decrease of thermopower between 1 and 2 GPa correlates with the increase of the hole concentration in the same pressure range (Fig. 2).

All changes occurring above 4 GPa in InSe are irreversible and reflect the destabilization of the layered structure. The first interesting fact is that we found that the sign of the Hall voltage changed from 4.2 to 4.7 GPa. Between these two pressures, the existence of instabilities in the Hall voltage prevented any accurate measurement. The observed change in the sign of the Hall voltage is the consequence of a carrier-type inversion induced by pressure. After this carrier-type inversion, the carrier concentration increases from \( 6.9 \times 10^{17} \) cm\(^{-3} \) at 4.7 GPa to \( 5.8 \times 10^{19} \) cm\(^{-3} \) at 7.2 GPa. Beyond 7.2 GPa we could not measure the Hall signal because the Hall signal became very weak. At 4.7 GPa a large decrease of the carrier mobility is also observed. However, the increase of the carrier concentration is the dominant effect producing the decrease we observed in \( \rho \).

Consistently with the irreversible increase of the electron concentration by 3–4 orders of magnitude, a drop of thermopower by one order of magnitude is observed in both n- and p-type InSe between 4 and 6 GPa, followed by a change of sign in p-InSe.

The destabilization of InSe layer-structure above 4 GPa is not yet well characterized as two competing mechanisms could be involved. On the one side, in this pressure range the system is close to the P–T line of the rhombohedral-to-monoclinic phase transition [32], that occurs by heating at about 100 °C in that pressure range. This transition involves a complete rearrangement of the intra- and inter-layer bonds. Local breaking of the layered structure can give rise to a large concentration of donor centers like those proposed in Ref. [16]. On the other side, in regions around dislocations the local pressure can be much higher [38] and the strain could be relaxed by a local transition to the rock salt phase, with metallic character. Independently of the actual mechanism, defects created by the instability of the layered phase have donor character, which in the case of p-InSe case first compensate the acceptors and subsequently produce the observed carrier-type inversion. The abrupt decrease of the mobility observed above 4.5 GPa, which reaches a value close to 1 cm\(^2/Vs \) beyond 6 GPa, is consistent with a sample with a very high concentration of defects. This picture is also in agreement with the blackening of the sample observed at 9 GPa due to the propagation of defects in InSe [38].

From reflectivity measurements [34], it can be estimated that the electron concentration at 8 GPa in n-type InSe is of the order of \( 10^{21} \) cm\(^{-3} \). The results shown in Fig. 3 are in agreement with the reflectivity measurements since an extrapolation of the electron concentration up to 8 GPa gives also a value close to \( 10^{21} \) cm\(^{-3} \). On the other hand, at 10.5 GPa a large drop of \( \rho \) is observed. The same change was observed before in n-type InSe, being a consequence of the phase-transition to a metallic NaCl-type phase [16]. From 9 to 12 GPa \( \rho \) decreases by a factor 40–50 (see Fig. 2). If we assume that the mobility remains nearly constant above 7.2 GPa, then from the decrease observed in \( \rho \) an electron concentration of the order of \( 4 \times 10^{22} \) cm\(^{-3} \) is estimated for our InSe sample in the metallic phase, a typical value for a metal. This estimation is only slightly higher than the nominal electron concentration in rock-salt InSe. If one...
assumes a free electron per primitive unit cell (the unpaired electron in the In-Se molecule), and considering a cubic cell parameter of 5.5 Å [34], the electron concentration would be about $2.5 \times 10^{22} \text{ cm}^{-3}$. A thermopower of 2 $\mu V/K$ is consistent with the metallic character of rock-salt InSe. On the assumption of a parabolic conduction band, and assuming the Seebeck coefficient to be given by the expression $\alpha = (\pi^2/3)(k_B/e)(k_B T/E_F)$, one can estimate the Fermi level to be about 3.5 eV above the conduction band minimum.

5 Conclusions

Hall effect, resistivity and thermopower measurements under pressure in p-type GaSe and InSe up to 12 GPa have revealed marked differences in the pressure behaviour of hole transport parameters. These differences can be satisfactorily understood on the base of previous ab initio calculations of their electronic structure and in particular, of the different evolution of the valence band maximum of each compound under pressure. Transport measurements beyond the pressure transition to the rock-salt phase in InSe have also contributed to a better characterization of its metallic nature.

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