Optical absorption of defect chalcopyrite and defect stannite ZnGa$_2$Se$_4$ under high pressure

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ABSTRACT

Optical absorption measurements at high pressure have been performed in two phases of the ordered-vacancy compound (OVC) ZnGa$_2$Se$_4$: defect stannite (DS) and defect chalcopyrite (DC). The direct bandgap energy of both phases exhibits a non-linear pressure dependence with a blueshift up to 10 GPa and a redshift at higher pressures. We discuss the different behavior of both phases in these two pressure ranges in relation to the pressure-induced order-disorder processes taking place at cation sites. Measurements performed in both phases on downstroke after increasing pressure to 22 GPa show that the direct bandgap energy of the recovered samples at room pressure was 0.35 eV smaller than that of the original samples. These results evidence that different disordered phases are formed on decreasing pressure, depending on the cation disorder already present in the original samples. In particular, we attribute the recovered samples from the original DC and DS phases to disordered CuAu (DCA) and disordered zincblende (DZ) phases, respectively. The decrease of the direct bandgap energy and its pressure coefficient on increasing disorder in the four measured phases are explained. In summary, this combined experimental and theoretical work on two phases (DC and DS) of the same compound has allowed us to show that the optical properties of both phases show a similar behavior under compression because irreversible pressure-induced order-disorder processes occur in all adamantine OVCs irrespective of the initial crystalline structure.

1. Introduction

ZnGa$_2$Se$_4$ is one of the most studied, and probably one of the most controversial semiconductors of the adamantine-type tetrahedrally-coordinated $A^{II}_2 B^{III}_2 X^{VI}_4$ family of ordered-vacancy compounds (OVCs) [1–3]. Contrary to most $A^{II}_2 B^{III}_2 X^{VI}_4$ adamantine OVCs, which crystallize at room conditions in the defect chalcopyrite (DC) structure (space group (S.G.) *I-4*, Fig. 1a), ZnGa$_2$Se$_4$ crystallizes mainly in the defect stannite (DS) structure, also known as defect famatinite (S.G. *I-42m*, Fig. 1b) [4–10], but also in the DC structure [11–16]. This has generated a considerable controversy regarding the true crystalline structure of this compound and its corresponding properties. Note that in the DC structure, cations and vacancies are completely ordered, being Ga atoms located at *2a* and *2c* Wyckoff sites, vacancies at *2b* Wyckoff sites, and Zn atoms at *2d* Wyckoff sites, while in the DS structure, there is a certain disorder at the cation-vacancy sites that leads up to 5 different phases or models previously discussed [14,17–19]; i.e, the DS structure is not a single structure but may correspond up to 5 different phases depending on the disorder [18,19].

The discrepancy in the structure of ZnGa$_2$Se$_4$ under room conditions comes from the lack of detailed information on crystal growth procedure and preparation of the studied samples in many studies. This information is important because phase diagram studies of ZnGa$_2$Se$_4$ reveal that it presents several order-disorder

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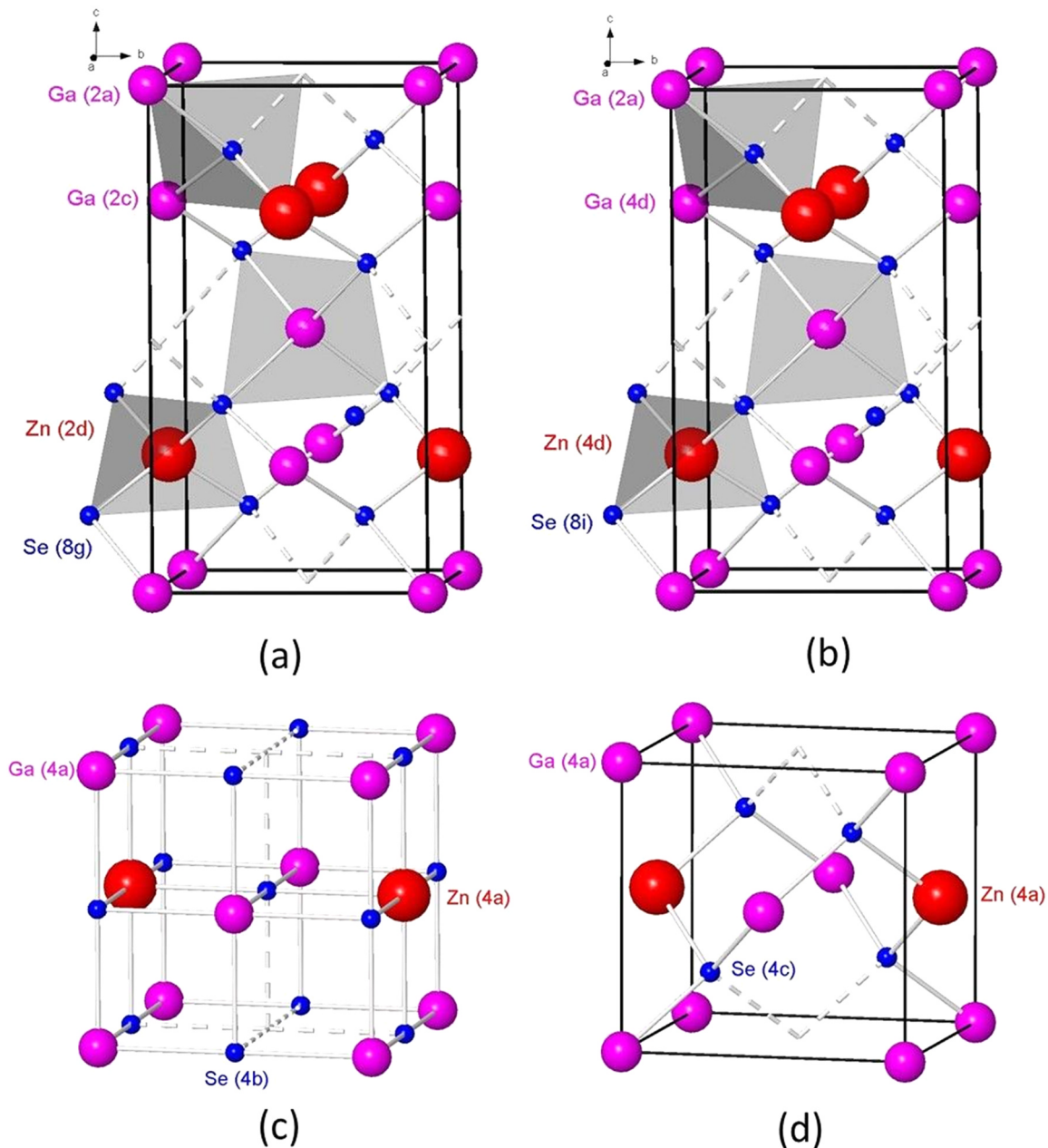*E-mail address:* osgohi@fis.upv.es (O. Gomis).

Fig. 1. (Color online) Structure of (a) defect chalcopyrite (DC) ZnGa$_2$Se$_4$, (b) defect stannite (DS) ZnGa$_2$Se$_4$, (c) defect rocksalt (DR) ZnGa$_2$Se$_4$, and (d) defect zincblende (DZ) ZnGa$_2$Se$_4$. Big red circles, medium magenta circles, and small blue circles correspond to Zn, Ga and Se atoms, respectively. Wyckoff sites are given in parenthesis.

transitions at relatively low temperatures that could affect its structure at room temperature [15,20,21]. In particular, it has been evidenced that details of crystal growth and sample preparation, like the maximum temperature reached in post-growth annealing treatment or the rate of decrease of temperature during the growth process or the annealing treatment, are crucial to understand the final structure of this compound at room conditions [21,22]. In fact, it is interesting to understand why ZnGa$_2$Se$_4$ can crystallize in both the DC and DS structures since it can affect many other $A^{II}B_2^{III}X_4^{VI}$ DC compounds that also exhibit a phase transition (PT) to the DS structure at high temperatures. This temperature-induced PT occurs because increasing temperature enhances atomic movements, thus promoting disorder at cation sites. In this sense, it is believed that on increasing temperature in ZnGa$_2$Se$_4$ the ordered cations at 2c and 2d sites of the DC structure mix together leading to a symmetry increase with both cations located at the 4d site of the DS structure. This temperature-induced disorder ($\approx 500\,°$C) [22] results in a PT

from the DC to a DS structure, which corresponds to model 2 of DS phases [18,19]. Furthermore, it has been shown that at much higher temperature a complete cation-vacancy disorder is induced, so a PT from the DS structure to the disordered zincblende (DZ, S.G. F-43m, Fig. 1d) structure takes place [23].

It has been argued that the presence of the DS phase at room conditions is common in many Zn-based $A^{II}B_2^{III}X_4^{VI}$ OVCs since the low mobility of Zn and the short time used for reducing the temperature during solid-state crystal growth favors the quenching of the high-temperature DS phase at room conditions. In other words, it is believed that the high-temperature DS phase stays metastable at ambient conditions in Zn-based $A^{II}B_2^{III}X_4^{VI}$ OVCs [22,24]. Furthermore, it has been shown that after proper thermal treatment of the DS structure of ZnGa$_2$Se$_4$ near 400 ºC (slowly decreasing temperature at a rate of near 1 º C/min), it is possible to get this compound in the more ordered DC structure [22,24,25]. This kinetics was not understood in the past and, consequently, there was no agreement

on the determination of the physical properties of $ZnGa_2Se_4$. Unfortunately, this controversy has hindered the studies of adamantine OVCs and prevented the practical use of this semiconductor; a tetrahedrally-coordinated semiconductor related to well-known III-V and II-VI semiconductors GaAs and ZnSe, respectively.

As regards the studies of the properties of $ZnGa_2Se_4$ under compression, an X-ray diffraction study in $DS-ZnGa_2Se_4$ showed that this semiconductor undergoes a pressure-induced PT to the disordered rocksalt structure (DR, S.G. *Fm−3m*, Fig. 1c) structure above 18 GPa [4]. On the other hand, several studies of Raman scattering have reported the pressure dependence of the Raman-active modes on $DS-ZnGa_2Se_4$ [9,16]. Thanks to our treatment of originally grown single crystals of the DS phase, we were able to synthesize single crystals of the DC phase after moderate heating and annealing and characterize the Raman scattering and optical absorption properties of both DS and DC phases at room conditions [25]. Consequently, we reported the pressure dependence of the Raman-active modes of both DC- and $DS-ZnGa_2Se_4$ and discussed the pressure-induced order-disorder processes taking place in both phases [26]. However, no study on the pressure dependence of the optical absorption edge in the two phases of $ZnGa_2Se_4$ has been reported yet to confirm the hypotheses stated in ref. [26].

Despite the lack of optical absorption studies of $ZnGa_2Se_4$ under compression, optical studies have been performed in other OVCs. Two recent works have reported the optical absorption edge of $DC-CdGa_2Se_4$ at different pressures up to 16 GPa [18,27]. In the first work, the strong non-linear pressure dependence of the direct bandgap energy in all adamantine OVCs at pressures up to 10 GPa was explained as due to a conduction band anticrossing (CBAC) at the Γ point of the Brillouin zone caused by two facts: i) the presence of ordered vacancies in adamantine OVCs and ii) the doubling of the unit cell along the *c* axis with respect to the zincblende structure [27]. In the second work, the optical absorption edge of $DC-CdGa_2Se_4$ was analyzed and showed that the strong non-linear decrease of the direct bandgap energy above 8 GPa in $DC-CdGa_2Se_4$ was due to the increase of cation disorder above that pressure. This increase in cation disorder was attributed to a gradual PT from the DC to the DS structure that occurs before the PT to the opaque metallic DR structure [18]. Optical absorption measurements on adamantine OVCs at high pressure have been performed also in $DC-HgGa_2Se_4$. It has been demonstrated that the direct bandgap energy shows a nonlinear pressure coefficient and that there are considerable changes in the bandgap energy at room pressure and its pressure coefficient for recovered samples due to the different degrees of disorder achieved after a high-pressure treatment [28]. More recently, it has been shown that the non-linear pressure dependence of the direct bandgap energy is also observed in sulfur-based OVCs, like $CdGa_2S_4$ and $HgGa_2S_4$ [29], thus confirming the hypothesis already published in Ref. [27].

To complete the study of the optical properties in the AGa_2Se_4 (*A*=Zn, Cd, Hg) family of OVCs, we report here an optical absorption study of both DC- and DS phases of $ZnGa_2Se_4$ at high pressures, which includes two upstrokes and two downstrokes. This work reports (to our knowledge) the first optical absorption study at high pressure of an OVC crystallizing in the DS structure; i.e. a sample originally grown with DS structure. Therefore, this work allows us to analyze in a single compound the similarities and differences between the optical properties of both DC and DS phases that appear in the adamantine $A^{II}B_2^{III}X_4^{VI}$ family of OVCs. In particular, it has allowed us to discuss the pressure-induced order-disorder processes taking place in the two phases of this controversial semiconductor. Finally, we want to highlight that this work allows clarifying the different bandgaps in OVCs with different degrees of cation-vacancy disorder and could open the door to studies of photoelastic and photoconductive properties in adamantine OVCs, which are expected to be more tunable than those observed in binary zincblende

and wurtzite semiconductors, like ZnO, ZnS, ZnSe, and CdS [30,31], especially now that the operating mechanism of the above-mentioned properties, related to undesired vacancies and other defects, is better understood [32].

2. Experimental details

$DS-ZnGa_2Se_4$ crystals were grown from its constituents ZnSe and Ga_2Se_3 by chemical vapor transport method using iodine as a transport agent [33] and are the same samples used in Refs. [4,9,26]. Chemical and structural analyses have shown the stoichiometric composition of the crystals with no spurious phases. Extensive experimental data on the structure of $DS-ZnGa_2Se_4$ (S.G. *I-42m*) can be found in ref.[4]. In particular, lattice and atomic parameters at room pressure are: a= 5.512 Å, c= 10.963 Å, Ga at *2a* sites, vacancies at *2b* sites, and Zn and Ga atoms mixed at *4d* sites, and Se atoms at *8i* sites with free parameters $x = 0.264$, $y = 0.264$, $z = 0.117$. On the other hand, $DC-ZnGa_2Se_4$ crystals used in this study were obtained from as-grown $DS-ZnGa_2Se_4$ by submitting them to controlled heating and cooling cycles in vacuum [25], following the procedure described in [22]. DC samples here studied are from the same batch studied in **Ref.** [26]. We have to stress that DC samples are not absolutely pure and contain a small proportion of the DS phase, as already discussed in **Ref.** [26]; however, from now on we will name this thermally treated sample as "DC sample" since the small proportion of DS phase should be negligible and does not affect the results discussed in the present work. We will show here that a high-pressure study of both DC and DS samples up to the same pressure value show different results.

Samples used in the optical absorption measurements had almost parallel faces with around 20 μm in thickness and 100×100 μm^2 in size. The samples were loaded together with a 16:3:1 methanol-ethanol-water mixture in the 250 μm diameter hole of an Inconel gasket inside a membrane-type diamond anvil cell. Ruby grains were used for pressure calibration [34]. High-pressure optical absorption experiments at room temperature were performed using the sample-in sample-out method and a micro-optical system [35] in combination with a tungsten lamp and an Ocean Optics spectrometer. Stray light was measured in the high absorption region of the sample for every spectrum and subtracted from the transmission spectrum. The experimental transmittance spectrum was scaled to fit the theoretical value of the transmittance in the spectral range through which the sample is transparent (an absorption coefficient of $\alpha = 0$). The theoretical transmittance T_{theor} is calculated by [36]:

$$T_{theor} = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} \tag{1}$$

where R is the reflectivity, α the absorption coefficient and d the sample thickness. The reflectance is obtained with [36]:

$$R = \left[\frac{n - n_0}{n + n_0} \right]^2 \tag{2}$$

where n is the refractive index of the sample and n_0 the refractive index of the methanol-ethanol-water pressure transmitting medium. The scaling procedure gives a corrected experimental transmittance T obtained by $T = c \cdot T_{theor}$ being c the correction factor.

Finally, the absorption coefficient α was determined from the corrected experimental transmittance T using Eq. (1) by:

$$\alpha = \frac{1}{d} \ln \left[\frac{(1 - R)^2}{2T} + \sqrt{\left[\frac{(1 - R)^2}{2T} \right]^2 + R^2} \right] \tag{3}$$

In our case, for DC- and $DS-ZnGa_2Se_4$, we have taken $d = 20$ μm, $n = 2.7$ [37] and $n_0 = 1.35$ [38]. The experimental direct bandgap

energy in both DS- and DC-ZnGa$_2$Se$_4$, as well as of the DCA and DZ phases latter commented, were obtained from the plot of the absorption coefficient, α, vs. photon energy, hν, by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ vs. hν plot to zero. An example is shown in the inset of Fig. 3 for DC-ZnGa$_2$Se$_4$.

3. *Ab initio* calculations

Total energy calculations were performed within the framework of the density functional theory (DFT) and the pseudopotential method using the Vienna ab initio simulation package (VASP) [39–42]. The exchange and correlation energy has been taken in the generalized gradient approximation (GGA) according to Perdew-Burke-Ernzerhof (PBE) prescription [43]. Details of total-energy calculations in the DC structure can be consulted in Ref. [27]. The set of plane waves employed extended up to a kinetic energy cutoff of 400 eV and a k-mesh of (4 ×4×4) was used with the primitive cell. Theoretical values of the lattice and atomic parameters of the simulated DC-ZnGa$_2$Se$_4$ (S.G. *I-4*) at 0 GPa (in this work and in Ref. [26]) are: $a = 5.6358$ Å, $c = 11.0823$ Å, Ga atoms at 2a sites, vacancies at 2b sites, Ga atoms at 2c sites, Zn atoms at 2d sites, and Se atoms at 8g sites with free parameters $x = 0.2581$, $y = 0.26486$, $z = 0.13276$. As expected [44], our theoretical values obtained with GGA-PBE functional slightly overestimate the experimental structural lattice parameters reported: $a = 5.496$ Å, $c = 10.99$ Å, and Se free parameters $x = 0.25$, $y = 0.25$, $z = 0.125$ [11]. As regards the DS structure, out of the five possible DS phases for OVCs discussed by Eifler et al. and Gomis et al. [14,17,18], samples of DS-ZnGa$_2$Se$_4$ correspond to model 2. This model has fractional atomic occupations so total energy calculations of this phase could not be performed.

4. Results and discussion

Since several upstrokes and downstrokes have been performed in the DC and DS samples, we will present and discuss from now on the results of the different upstrokes and downstrokes in different subsections.

4.1. First upstroke

Figs. 2 and 3 show the pressure dependence of the optical absorption spectra in DS- and DC-ZnGa$_2$Se$_4$ up to 18 GPa, respectively. It can be observed that the absorption edge shows a pressure-induced blueshift (redshift) below (above) 10 GPa for both phases. As already commented, similar blueshifts and redshifts were found in DC-CdGa$_2$Se$_4$, DC-HgGa$_2$Se$_4$, DC-CdGa$_2$S$_4$, and DC-HgGa$_2$S$_4$ [27–29]. From Fig. 2, the direct allowed nature of the bandgap in DS-ZnGa$_2$Se$_4$ at low pressures is consistent with the high value of the absorption coefficient, α, its steep increase with photon energy, hν, and the linear character of the $(\alpha h\nu)^2$ vs. hν plot at high energies. This result agrees with the studies of the optical absorption edge in DS-ZnGa$_2$Se$_4$ at room pressure [45–47]. A similar evolution is observed for the optical absorption edge of DC-ZnGa$_2$Se$_4$ (see Fig. 3).

Fig. 4 shows the pressure dependence of the experimental direct bandgap energy in DS- and DC-ZnGa$_2$Se$_4$, as obtained by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ vs. hν plot to zero. It can be observed that the direct bandgap energy of the DC sample is 0.1 eV higher than that of the DS sample. This is an expected result because cation disorder in OVCs, like CdIn$_2$Se$_4$ [48] and DC-CdGa$_2$Se$_4$ [18,27], results in a decrease of the direct bandgap energy. Moreover, a difference close to 0.13(3) eV was observed between DC- and DS-HgGa$_2$Se$_4$ near room conditions [28]. At low pressures, the direct bandgap energy for DC- and DS-ZnGa$_2$Se$_4$ increases with an experimental pressure coefficient of 51(4) meV/GPa and 45(4) meV/GPa, respectively. It can be also observed that the experimental direct bandgap energy of both DC- and DS-ZnGa$_2$Se$_4$
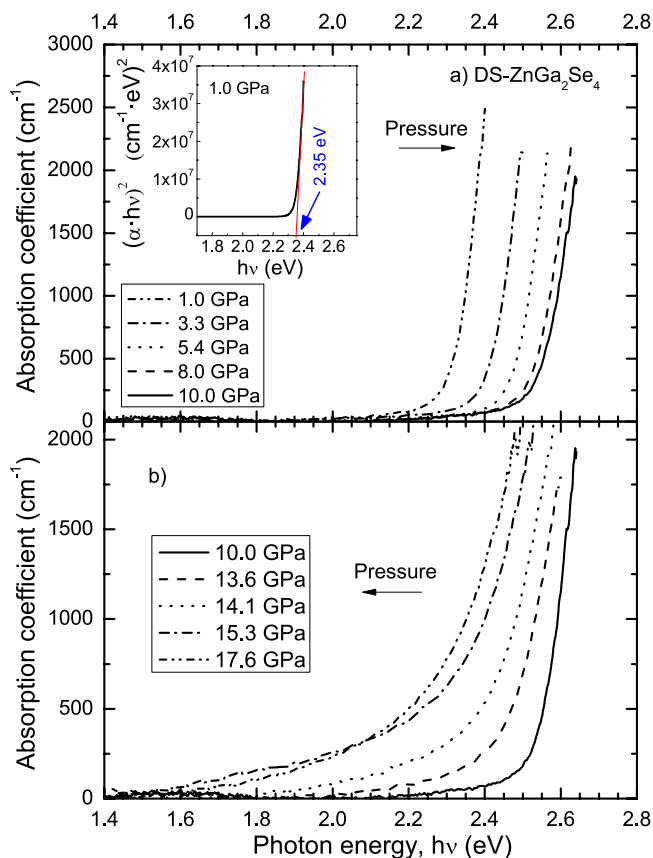
Fig. 2. (Color online) Absorption edge of DS-ZnGa$_2$Se$_4$ on increasing pressure (a) up to 10.0 GPa and (b) from 10.0 up to 17.6 GPa. Inset shows a plot of $(\alpha \cdot h\nu)^2$ vs. hν where the tangent method is applied to estimate the direct bandgap energy of DS-ZnGa$_2$Se$_4$ from the absorption coefficient at 1.0 GPa.

has a strong non-linear pressure dependence up to 8 GPa resulting in a red shift (negative pressure coefficient) above 10 GPa, as already commented. Our theoretical ab initio calculations for the pressure dependence of the direct bandgap energy in DC-ZnGa$_2$Se$_4$ (see solid line in Fig. 4) agree very well at low pressures with experimental data and confirm the non-linear behavior of the direct bandgap energy. Note that theoretical DFT calculations of the direct bandgap energy of the DC structure are underestimated with respect to the real band gap energy, so they have been properly shifted upwards to make them coincide with the experimentally estimated direct bandgap energy at room pressure. Our ab initio calculations yield a pressure coefficient of 50(4) meV/GPa at low pressures for DC-ZnGa$_2$Se$_4$ in good agreement with experimental results. We have also added in Fig. 4 theoretical calculations of the indirect Γ-Z band gap for the DC phase plotted by a dash-dotted line. These calculations show that there is not pressure-induced direct-indirect band gap crossing in the calculated pressure range for DC-ZnGa$_2$Se$_4$.

In previous works, the non-linear behavior of the direct bandgap energy was proposed to be a general feature common to all adamantine OVCs. It occurs due to a CBAC at the Γ point of the Brillouin zone caused by the presence of ordered vacancies in the crystalline structure of adamantine OVCs, and the doubling of the unit cell along the c axis with respect to the zincblende structure. Such CBACs have been observed in several OVCs, including Se-based OVCs, such as DC-CdGa$_2$Se$_4$, DC-HgGa$_2$Se$_4$, β-Ga$_2$Se$_3$, and S-based OVCs, such as DC-CdGa$_2$S$_4$, DC-HgGa$_2$S$_4$ [18,27–29] and proposed to occur in α′-Ga$_2$S$_3$ [49]. In the following, we will see that our calculations for DC-ZnGa$_2$Se$_4$ agree with previous ones on OVCs with DC structure and show that the non-linear pressure dependence of the direct bandgap energy is also caused by the CBAC at the Γ point of the Brillouin zone
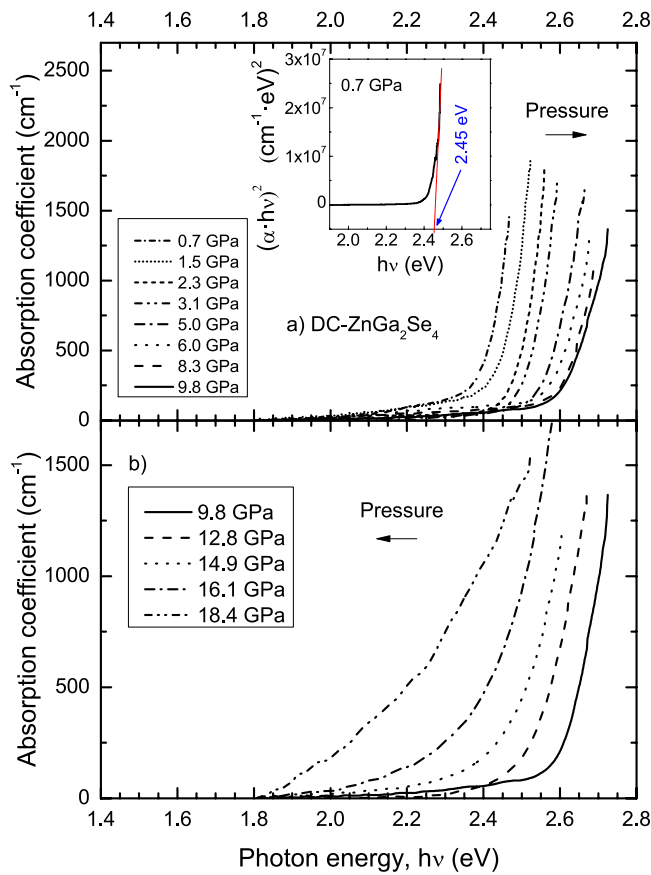
Fig. 3. (Color online) Absorption edge DC-ZnGa$_2$Se$_4$ on increasing pressure (a) up to 9.8 GPa and (b) from 9.8 up to 18.4 GPa. Inset shows a plot of $(\alpha \cdot h\nu)^2$ vs. $h\nu$ where the tangent method is applied to estimate the direct bandgap energy of DC-ZnGa$_2$Se$_4$ from the absorption coefficient at 0.7 GPa.
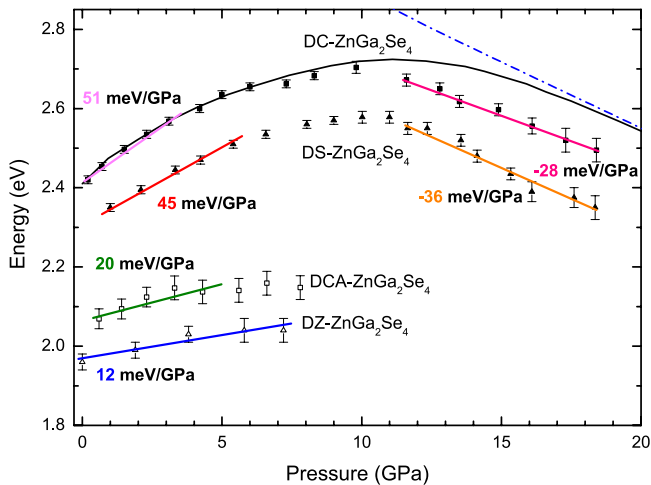

Fig. 4. (Color online) Pressure dependence of the band-gap energy in the different phases of ZnGa$_2$Se$_4$. Solid squares and triangles with error bars correspond to experimental values for the DC and DS phases, respectively, while open squares and triangles with error bars correspond to experimental values for the DCA and DZ phases, respectively. Experimental values of pressure coefficients of the direct bandgaps at low pressure (in the DC, DS, DCA and DZ phases) and at high pressure (in the DC and DS phases) are also shown. Colored solid straight lines are a guide to the eye for establishing the slopes of the bandgaps in the different structures of ZnGa$_2$Se$_4$. Theoretical calculations of the direct band gap for the DC phase are given by a solid line. Theoretical calculations of the indirect Γ-Z band gap for the DC phase are plotted by a dash-dotted line. All calculated energies are upshifted to match the experimental direct band-gap energy at room pressure.
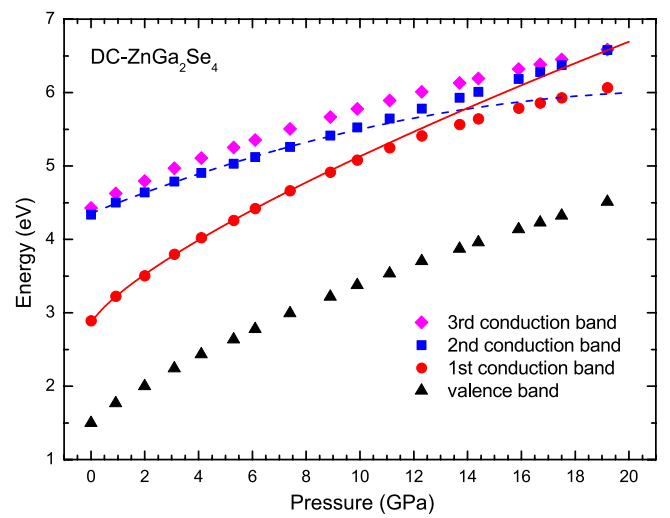

Fig. 5. (Color online) Theoretical pressure dependence of the energies of the topmost valence band and the lowest conduction bands at the Γ point for DC-ZnGa$_2$Se$_4$ (symbols). Solid (dashed) lines correspond to the expected pressure dependence of the first (second) conduction band energy in absence of band anticrossing.

caused by the presence of ordered vacancies in adamantine OVCs. Moreover, it is also the cause for the decrease of the direct bandgap energy in DC-ZnGa$_2$Se$_4$ at high pressure. The same mechanism is expected to occur in DS-ZnGa$_2$Se$_4$, which has not been simulated, to explain the strong non-linear pressure dependence and even the decrease of the direct bandgap energy of this OVC at high pressure.

To understand the strong non-linear pressure dependence of the direct bandgap in DC-ZnGa$_2$Se$_4$, we have studied the behavior of the electronic band structure as a function of pressure. Fig. 5 shows the pressure dependence of the theoretical energy of the valence band maximum (VBM) and the three lowest conduction bands (CBs) at the Γ point. They are named hereafter 1st CB (the lowest in energy at room pressure), 2nd CB, and 3rd CB.

We have found a CBAC of the two lowest CBs of DC-ZnGa$_2$Se$_4$ above 10 GPa (see Fig. 5), as that found for the first time in Ref. [27]. The CBAC was also found later in other Se-based OVCs, like DC-CdGa$_2$Se$_4$, DC-HgGa$_2$Se$_4$, and β-Ga$_2$Se$_3$ [27]. Solid and dashed lines in Fig. 5 show the expected pressure dependence (in a tentative way) of the energy of the first and second CBs in absence of CBAC, respectively. Additional evidence of the CBAC between the 1st and 2nd CBs in DC-ZnGa$_2$Se$_4$ can be found in the totally reversed atomic character shown by both bands between room pressure and high pressure (close to 20 GPa), as represented in Figs. 6b and 6c, respectively. The reason for the occurrence of the CBAC is that atomic characters of the different electronic bands in DC-ZnGa$_2$Se$_4$ determine their respective pressure coefficients, as it has been found in other OVCs, such as CdIn$_2$Se$_4$ [23].

The strong pressure dependence of the VBM, that is responsible for the observation of the strong change of pressure coefficient of the direct bandgap in OVCs, can be understood from its atomic character. In DC-ZnGa$_2$Se$_4$, the ordered vacancy occupies the 2b Wyckoff position so each Se only bonds with two Ga in 2a and 2c positions and one Zn in 2d position. Therefore, Se atoms show three covalent sp^3-type bonds and a fourth dangling bond pointing to the ordered vacancy in a tetrahedral configuration. This configuration is consistent with theoretical calculations predicting that the VBM is mainly dominated by the p orbital character of Se (corresponding to the non-bonding electron of the dangling bond) with minor contribution of p-d orbitals from other atoms (Figs. 6a and 7a). Consequently, the strong pressure dependence of the VBM under pressure is due the strong compressibility of the Se-vacancy distance (Fig. 8) that leads to the strong repulsion between the electronic levels of the VBM
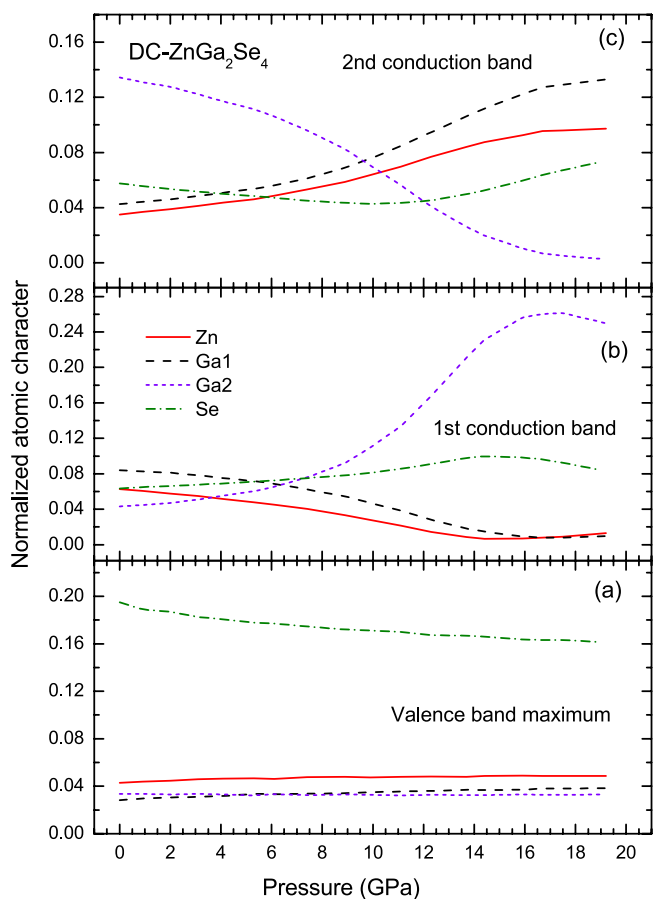
Fig. 6. (Color online) Theoretical pressure dependence of the atomic character of the (a) valence band maximum, (b) first, and (c) second conduction band at the Γ point in DC-ZnGa$_2$Se$_4$. Ga1 corresponds to the Ga in 2c Wyckoff position and Ga2 is the Ga in 2a Wyckoff position, according to Fig. 1.

associated to the dangling bonds of Se atoms surrounding the vacancy. In this context, we have to note that in a previous paper regarding CdGa$_2$S$_4$ and HgGa$_2$S$_4$ we offered a different explanation for the character of the VBM [29]. There, it was commented that the VMB had s character of S (typical of non-bonding lone electron pairs) and that S formed three p-type covalent bonds with Ga and Cd (Hg) atoms. Such an explanation is at odds with previous and present calculations of Se-based OVCs, where the VBM shows Se p character. To solve this controversy, we have recalculated the electronic bands of DC-CdGa$_2$S$_4$ and found that indeed the VBM shows S p character (Fig. 7b). Therefore, we can safely conclude that all S- and Se-based AB_2X_4 OVCs show three covalent sp^3-type bonds and a fourth dangling bond pointing to the vacancy in a tetrahedral configuration. Moreover, we can conclude that the strong pressure coefficient of the VBM in OVCs comes from the strong compressibility of the dangling bonds formed by p-type electrons that pushes up the top electronic levels of the VBM in a larger way than in usual covalent sp^3-type tetrahedral semiconductors without dangling bonds.

On the other hand, the pressure dependence of the 1st and 2nd CBs can also be understood in terms of their atomic characters. The strong pressure dependence of the 1st CB at low pressures is given by the high s cation (Zn and Ga1) contribution (Fig. 6b) since it is well known that anti-bonding s cation levels give rise to strong pressure coefficients of the1st CB due to the strong repulsion between bonding and antibonding cation s levels. In this context, the small pressure coefficient of the 2nd CB at low pressures can be ascribed to the high Ga2 contribution but small Zn and Ga1, as well as Se contributions (Fig. 6c) due to the smaller compression of the

Ga2-Se bond than of the Zn-Se and Ga1-Se bonds along the whole pressure range (see Fig. 8).

Evidence of the CBAC between the two lowermost CBs above 10 GPa can be observed in the totally reversed change of the atomic character between these two CBs between low pressures and high pressures close to 20 GPa (Figs. 6b and 6c). Almost no change occurs in the atomic character (p orbital of Se) of the VBM in the whole pressure range (Fig. 6a). On the contrary, a considerable change of the atomic character of the two lowermost CBs occurs at HP (Figs. 6b and 6c). At low pressures the 1st CB was dominated by Ga1 (Ga at 2c Wyckoff position), lower contribution of Se and Zn and minor contribution from s orbital of Ga2 (Ga at 2a Wyckoff position). In contrast, at low pressures, the 2nd CB is mainly contributed by Ga2, lower contribution of Se and a small contribution from s character of Ga1 and Zn. At pressures above 10 GPa, both CBs reverse their atomic characters; a characteristic feature of the CBAC already observed in other OVCs.

It can be observed in Figs. 2 and 3 that there is a strong decrease of the optical absorption edge in both DC and DS phases above 10 GPa. We have checked that the optical absorption edge still corresponds to a direct bandgap in both DC and DS phases above 10 GPa. Above this pressure, the direct bandgap energy for DC- and DS-ZnGa$_2$Se$_4$ decreases with an experimental pressure coefficient of −28(3) meV/GPa and −36(3) meV/GPa, respectively (Fig. 4). As observed in Fig. 4, the decrease of the experimental direct bandgap energy in DC-ZnGa$_2$Se$_4$ is similar to that predicted by our calculations (−27(2) meV/GPa) and occurs at a smaller pressure than in theoretical calculations. These features have been also found in other OVCs with DC structure [18,27–29] and attributed to the pressure-induced order-disorder processes occurring in OVCs. Although the CBAC predicts the decrease of the bandgap energy above a certain pressure, it does not correctly reproduce the experimental values nor the onset pressure above which the decrease is produced.

We consider that the same explanation given for DC-ZnGa$_2$Se$_4$ in the above paragraph is valid to explain the strong decrease of the direct bandgap energy in DS-ZnGa$_2$Se$_4$ above 10 GPa. In fact, we believe that pressure-induced disorder occurs above certain pressure in all OVCs irrespective of the initial disorder degree (see all possible structures of OVCs with AB_2X_4 composition in Ref. [27]), since all of them tend to undergo a PT to a fully disordered rocksalt (DR) structure with a complete mixture of cations and vacancies at the same Wyckoff site, as evidenced in previous studies [4,50]. Support for this claim is not only provided by the similar behavior of the optical absorption edge of DC- and DS-ZnGa$_2$Se$_4$ at high pressure, but also by the similar behavior observed for the Raman scattering of DC and DS-ZnGa$_2$Se$_4$ up to 18 GPa [26].

Examples of the gradual increase of cation-cation and cation-vacancy disorder occurring in DS-ZnGa$_2$Se$_4$ at high pressure can be found in the pictures taken at different pressures during upstroke (see Fig. 9). The appearance of dark linear defects, which are precursors of the PT from the DS to the DR phase, can be observed around 14 GPa in Fig. 9. Furthermore, the DS phase becomes largely unstable with respect to the DR phase above 16.1 GPa and large dark regions appear in the sample [51,52]. However, the optical absorption edge can still be measured in some parts of the sample. This is not the case above 18.4 GPa, since the sample is almost completely darkened at this pressure, and the optical absorption could not be measured anymore above that pressure. Above 20 GPa, the phase transition to the DR structure is complete and the sample is completely opaque. A similar situation was observed for the DC sample (not shown). In this context, we have noted in a recent paper regarding Raman scattering measurements in DC- and DS-ZnGa$_2$Se$_4$ that the PT to the DR phase is not completed in the DC sample at 20 GPa and it is necessary to pressurize till 25 GPa to fully transform the DC sample to the DR phase [26]. Since we have pressurized DC-
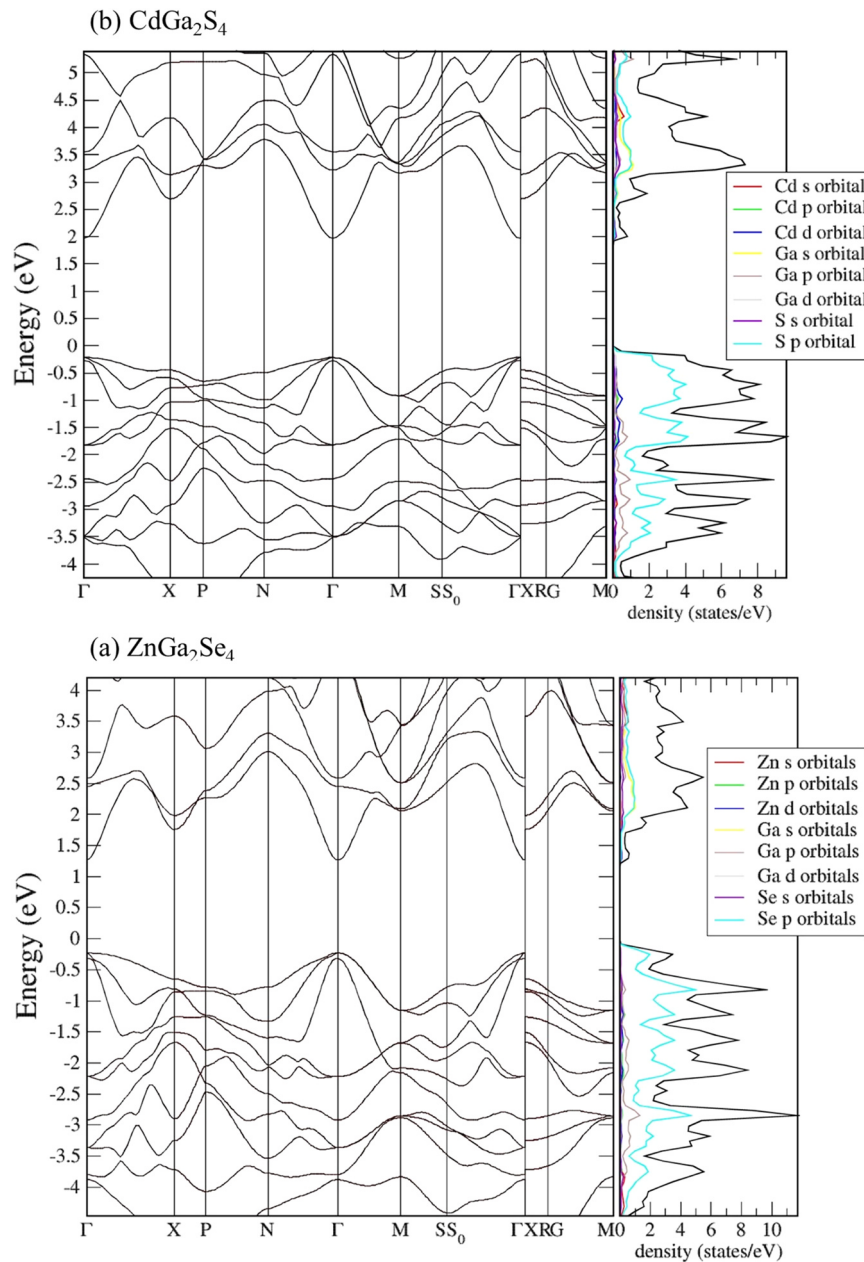
Fig. 7. (Color online) Electronic band structure and density of states (DOS) for (a) $ZnGa_2Se_4$ and (b) $CdGa_2S_4$ calculated at 0 GPa. Solid black line at the DOS represents the total DOS.

$ZnGa_2Se_4$ only to 22 GPa in this work our DC sample has not undergone a complete PT to the DR phase.

It must be stressed that the appearance of dark linear defects in semiconductors as precursors of the PT from a tetrahedrally-co-ordinated structure to an octahedrally-coordinated, metallic structure, such as the rocksalt phase is already known in a number of compounds. The appearance of such dark linear defects on certain parts of the sample is not necessarily related to pressure gradients in the DAC, but likely related to the existence of overpressure in certain parts of the sample that could be related to the existence of point or linear defects in the sample either intrinsic or caused by pressurization, as it was shown for InSe [53].

4.2. First downstroke

One of the questions to be answered in high-pressure studies of OVCs is whether the pressure-induced order-disorder processes are irreversible even before undergoing the PT to the DR phase. X-ray diffraction and Raman scattering measurements in DC-$CdGa_2Se_4$ suggested that the order-disorder processes in this compound are clearly non-reversible. In fact, a DZ phase was obtained on decreasing pressure from 20 GPa, pressure at which the DR phase was found [18,54]. For ZnGa2Se4, a previous Raman work in DC- and DS-$ZnGa_2Se_4$ concluded that DC-$ZnGa_2Se_4$ returns to a DC phase or to a mixture of DC and disordered CuAu-like (DCA) phases provided that the sample is subjected to 20 GPa, since at that pressure the order-disorder PT to the DR structure is not completed [26]. Similarly, the DS phase returns to the DS phase if the phase transition to the DR structure is not completed. However, if the pressure is high enough to fully transform DC- and DS-$ZnGa_2Se_4$ into the DR structure, the disorder process is completely irreversible and on decreasing pressure the sample results in the completely disordered zincblende (DZ) phase [26].
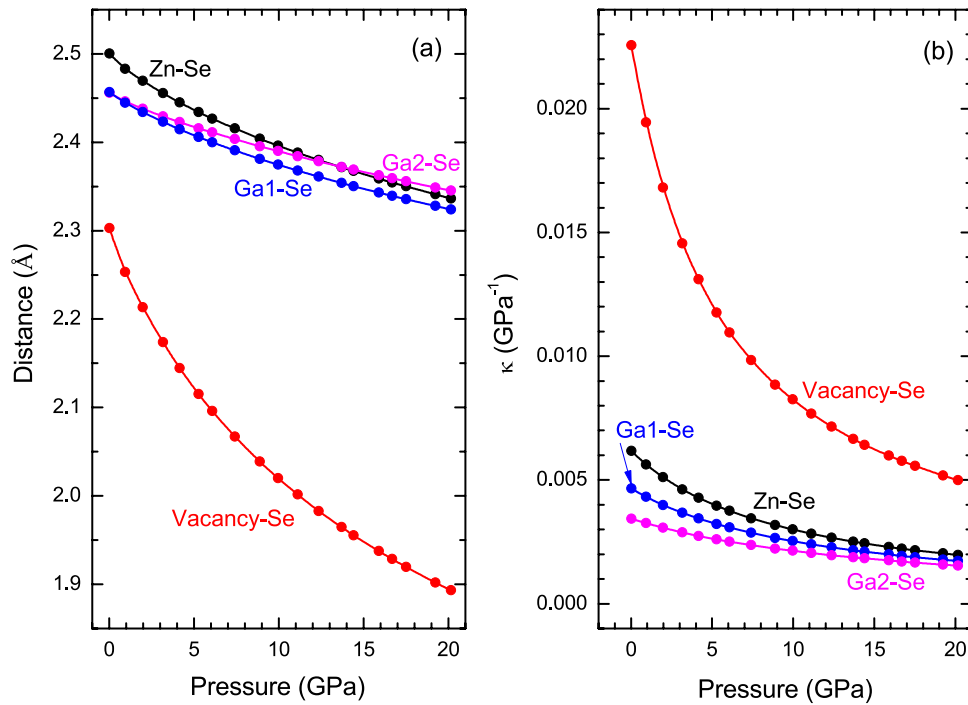
Fig. 8. (Color online) Pressure dependence of the (a) calculated cation-anion and vacancy-anion distances, and (b) distance compressibilities in DC-ZnGa$_2$Se$_4$. Ga1 corresponds to the Ga in 2c Wyckoff position and Ga2 is the Ga in 2a Wyckoff position, according to Fig. 1.

In order to check the reversibility of the pressure-induced disorder processes in ZnGa$_2$Se$_4$, we have measured the optical absorption edge of DC- and DS-ZnGa$_2$Se$_4$ on downstroke from 22 GPa till almost ambient pressure. As already commented, the pressure of 22 GPa is well above the phase transition pressure to the DR structure in DS-ZnGa$_2$Se$_4$, but still not enough to get the full transformation into DC-ZnGa$_2$Se$_4$. Fig. 10 shows selected pictures taken at different pressures after the first upstroke in DS-ZnGa$_2$Se$_4$ up to 22 GPa. It can be observed that the sample recovers transmittance in the visible range on downstroke below 5 GPa, thus showing a strong hysteresis in the DS-to-DR PT. The sample becomes clearer on decreasing pressure down to 1.2 GPa, but some dark linear defects remain because of the first pressure cycle. The difference in color of the sample before (green-yellow) and after (dark red) the first upstroke accounts for a decrease of the direct bandgap of around 0.3 eV in the recovered sample. The decrease of the bandgap energy in the recovered samples of both initial DC and DS samples is attributed to the pressure-induced disorder process, as already commented in a
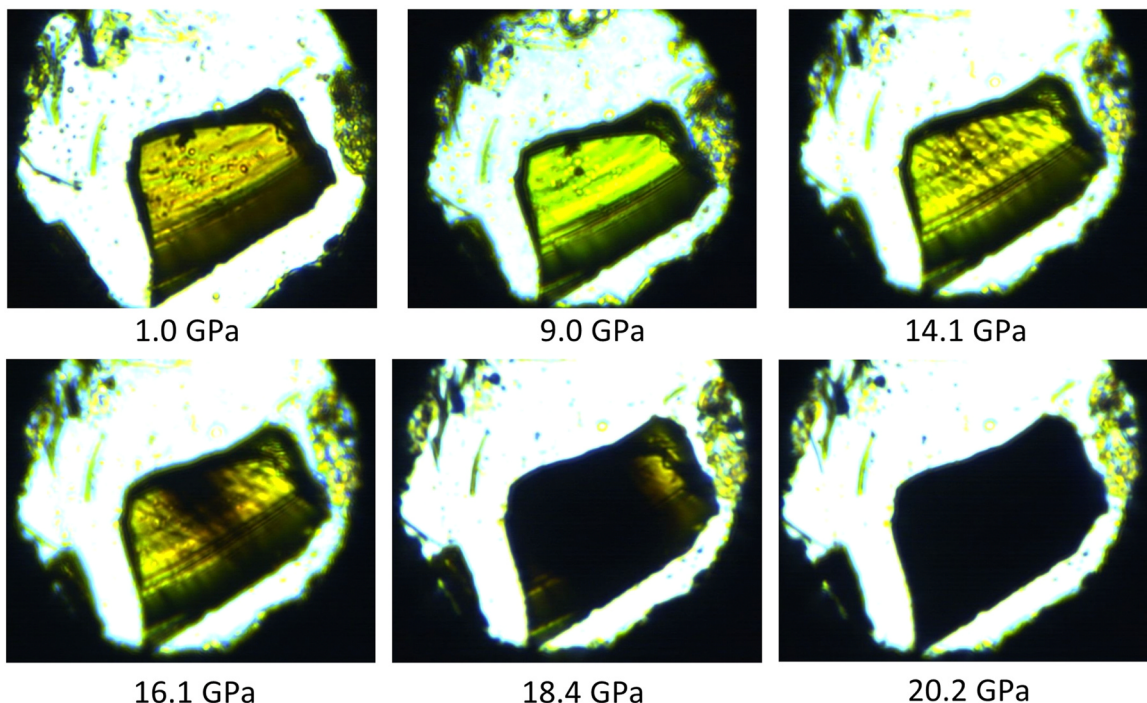

Fig. 9. (Color online) Sample photographs obtained at different pressures during the first upstroke in DS-ZnGa$_2$Se$_4$.
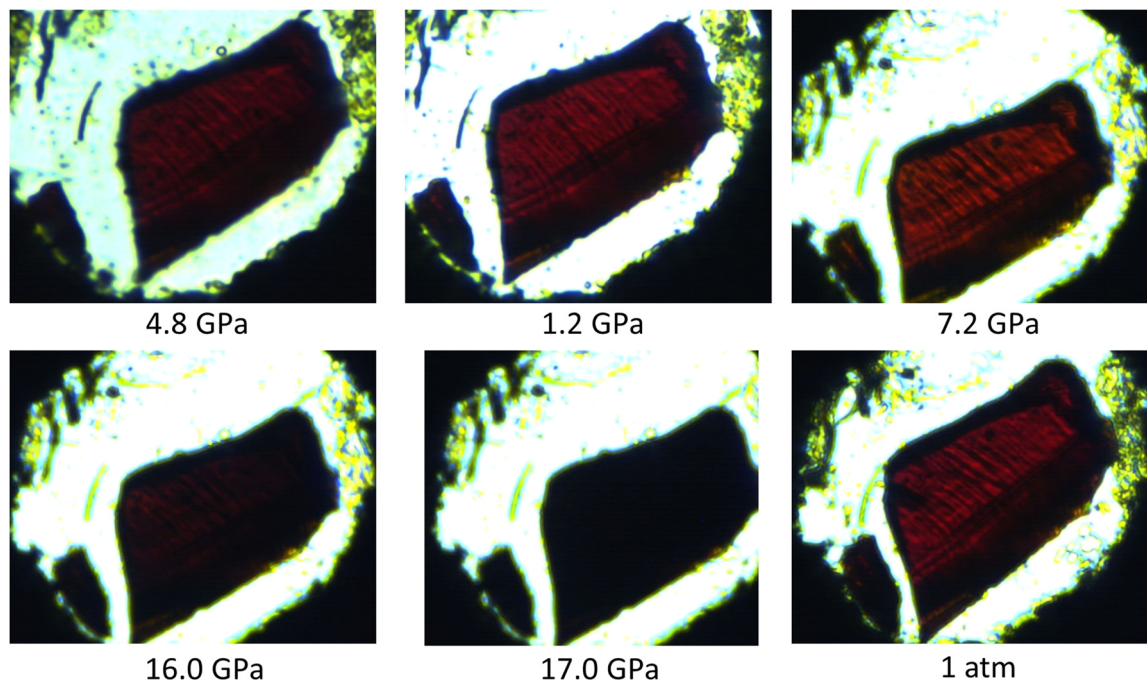
Fig. 10. (Color online) Sample photographs obtained consecutively at selected pressures during the first downstroke (4.8 and 1.2 GPa), the second upstroke (7.2, 16.0, and 17.0 GPa), and the second downstroke (1 atm) in DS-ZnGa$_2$Se$_4$.

previous high-pressure optical study of DC-CdGa$_2$Se$_4$ where a PT to the DZ phase is reported [18]. We must note that a decrease of the direct bandgap energy in recovered samples has also been found in pressurized ordered *ABX*$_2$ chalcopyrite-type compounds. This can be understood because they also undergo an order-disorder PT to a DR phase, like in CuAlSe$_2$ above 12 GPa [55], and on decreasing pressure a DZ structure should be obtained with smaller band gap than that of the chalcopyrite phase due to intrinsic defects. Note that a comparable but smaller decrease of the bandgap was also found in CdGa$_2$Te$_4$ after a high temperature treatment. In this case, the disorder at cation sites causes the decrease of the bandgap energy from 1.5 eV in the ordered DC structure to 1.4 eV in the DZ phase [23]. Therefore, we interpret that the strong decrease of the direct bandgap energy in both DC- and DS-ZnGa$_2$Se$_4$ on downstroke from 22 GPa evidences the formation of phases with a larger cation disorder than the one present in the original samples.

The reason for the decrease of the direct bandgap energy and its pressure coefficient in the series DC-DS-DCA-DZ of ZnGa$_2$Se$_4$ (also applied to other OVCs) can be explained by the increase of the cation-anion bond distances as disorder increases due to the slightly larger volume per formula unit with increasing disorder [56], as already suggested for CdGa$_2$Se$_4$ [18]. In this argument, disorder (that increases the cation-anion distances) acts inversely to pressure (that decreases the cation-anion distances). Therefore, disorder leads to a larger decrease of the CBM energy than the VBM energy and consequently to a decrease of the direct bandgap energy, while pressure leads to a larger increase of the of the CBM energy than of the VBM energy, thus leading to an increase of the bandgap energy at low pressures. The enlargement of the cation-anion distances (at a given pressure) in more disordered structures is reflected in the increase of the Raman frequency of the breathing mode, a highly anharmonic vibrational mode characteristic of OVCs [57,58], as observed at room pressure in DS- and DC-ZnGa$_2$Se$_4$ [26] and in DC- and DZ-CdGa$_2$Se$_4$ [18].

The increase of the anion-cation distance on increasing disorder (at a given pressure) allows also explaining why the direct bandgap energy of the DZ phase is smaller than that of the DCA phase (and much smaller than the DS and DC phases) since the cation-vacancy

disorder is maximum for the DZ phase [18]. Note that the smaller bandgap of the recovered DC sample (0.3 eV below that of the DC phase) than that of the original DS phase (0.1 eV below that of the DC phase) provides additional support for the tentative assignment of the recovered DC phase to the DCA phase, with a larger disorder at cation sites than the DS phase [27]. Similarly, the smaller bandgap of the recovered DS sample (0.4 eV below that of the DC phase) provides support for the tentative assignment of the recovered DS sample to the DZ phase. Note that the difference between the direct bandgap energy of the DC and DS (DZ) phases in HgGa$_2$Se$_4$ was around 0.15 eV (0.25 eV) [26]. This result is in relatively good agreement with our present results on ZnGa$_2$Se$_4$; however, there is much better agreement between pressure coefficients, as commented in the next paragraph.

We tentatively attribute the nature of the structure in the recovered sample of the initial DS sample to the DZ structure and that of the recovered sample of the initial DC sample to the DCA structure (see all possible structures of *AB*$_2$*X*$_4$ OVCs in Ref. [27]). Further arguments in support of these hypotheses are given below. In this context, we must note that the structures here proposed for the recovered samples of the original DC and DS phases are slightly different to those proposed in a previous work on HgGa$_2$Se$_4$ [28]. The reason is that the DC phase usually undergoes a PT in OVCs above 10–12 GPa to the DS phase and above 20–25 GPa to the DR phase; therefore, a DC phase subjected to around 15 GPa, as in Ref. [26], is recovered in a DS phase; however, when pressure goes above 20 GPa (even before reaching the DR phase) the disorder is much bigger than that in the DS phase and a DCA phase is likely to be formed as is here the case for DC-ZnGa$_2$Se$_4$ pressurized to 22 GPa. In this context, we must note that if DC-ZnGa$_2$Se$_4$ were pressurized beyond 25 GPa, the resulting DR phase would undergo a PT on downstroke to a DZ phase. In other words, due to the irreversibility of the order-disorder PT once a full disorder is obtained, like in the DR phase, no possible intermediate phase with any kind of order can be obtained on downstroke. The only possibility on downstroke is to obtain a fully disordered phase as the DZ [27].
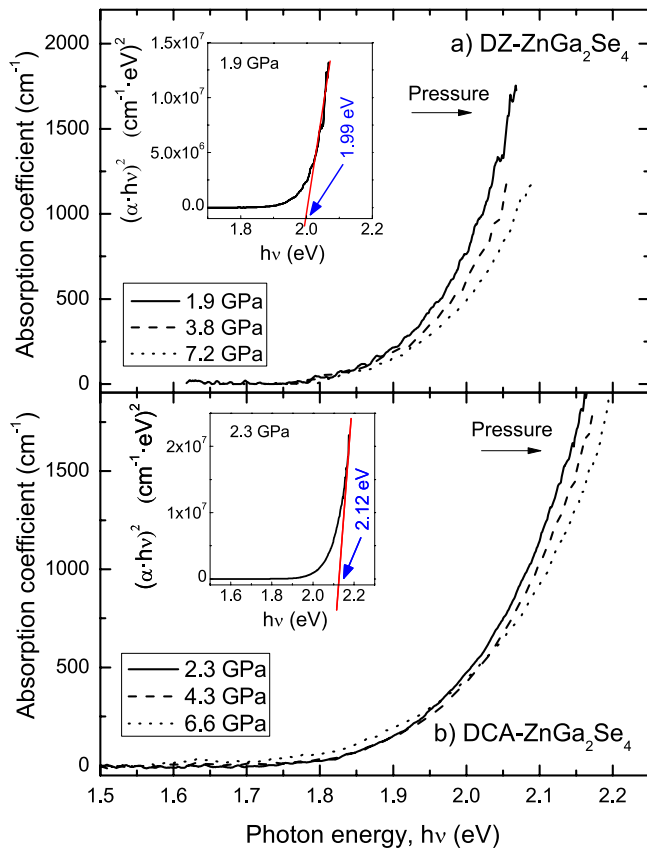
Fig. 11. (Color online) Pressure dependence of the absorption edge of the recovered samples of DZ-ZnGa$_2$Se$_4$ (a) and DCA-ZnGa$_2$Se$_4$ (b), obtained after decreasing pressure from 22 GPa in original DS and DC samples. Insets show a plot of $(\alpha \cdot h\nu)^2$ vs. $h\nu$ where the tangent method is applied to estimate the direct bandgap energy of DZ-ZnGa$_2$Se$_4$ from the absorption coefficient at 1.9 GPa and of DCA-ZnGa$_2$Se$_4$ at 2.3 GPa.

4.3. Second upstroke

Since the phases of the recovered samples (DCA and DZ) on downstroke from 22 GPa are different from the original (DC and DS) samples, we have further performed optical absorption measurements at high pressure in the new phases. Fig. 11 shows the pressure dependence of the optical absorption edge in the recovered DCA- and DZ-ZnGa$_2$Se$_4$ samples. From the optical absorption edges of the DCA and DZ phases we have obtained the direct bandgap energy as a function of pressure by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ vs. $h\nu$ plot to zero absorption. The direct bandgap energies of the DCA and DZ phases are shown in the lower part of Fig. 4 with open squares and triangles, respectively. Note that we have only obtained estimated values for the direct bandgap energy of DCA- and DZ-ZnGa$_2$Se$_4$ up to about 8 GPa because at higher pressures the absorption edge has a big tail due to defects precursors of the PT to the DR phase and prevent us to obtain with reasonable accuracy the bandgap energy by extrapolation.

On one hand, it can be observed that the extrapolated values of the direct bandgap energy in both DCA and DZ phases near zero pressure are about 0.3 eV smaller than their DC and DS phases, as already commented. Additionally, the extrapolated values of the direct bandgap energy in both DCA and DZ phases near zero pressure differ by about 0.1 eV, being smaller the direct bandgap of the DZ phase. On the other hand, the pressure coefficient of the direct bandgap of both DCA- and DZ-ZnGa$_2$Se$_4$ at room pressure is estimated from a linear fit to be around 20(5) meV/GPa and 12(3) meV/GPa, respectively. These pressure coefficients are much smaller than those of the original DC and DS phases at room pressure. In fact, they

are also much smaller than the pressure coefficients of binary zincblende-type compounds, like zincblende ZnSe (70 meV/GPa) [59,60].

The smaller pressure coefficient of the direct bandgap energy in the disordered DCA and DZ phases than in the DC and DS phases is due to the mixture of the two lowermost CBs of the DC and DS phases to give the lowermost CB in the DCA and DZ structures [18]. Since the second CB of the DC and DS phases has a much smaller absolute pressure coefficient than the first CB up to around 12 GPa, the resulting lowermost CB in the DCA and DZ structures exhibits a much smaller absolute pressure coefficient than in the DC and DS phases and consequently a smaller pressure coefficient of the direct bandgap. In other words, the pressure coefficient of the direct bandgap in OVCs must decrease with the increase of cation-vacancy disorder. According to this argument, a larger pressure coefficient of the direct bandgap energy would be expected for the DCA phase than for the DZ phase, as it is indeed found: 20(5) meV/GPa for the DCA phase and 12(3) meV/GPa for the DZ phase. Moreover, the value of the pressure coefficient for DZ-ZnGa$_2$Se$_4$ is in very good agreement with that found for DZ-HgGa$_2$Se$_4$ (7 meV/GPa). Moreover, the value found for DCA- ZnGa$_2$Se$_4$ is quite different to that of DS-ZnGa$_2$Se$_4$ and even smaller than that found for DS-HgGa$_2$Se$_4$. Therefore, the above results give support to our assignments of the structures of the recovered samples on downstroke.

As observed in Fig. 11, on further increasing pressure during a second upstroke, we could measure the pressure dependence of the optical absorption edge of DCA and DZ phases up to almost 8 GPa. At higher pressures, the samples darken again thus preventing an accurate measurement of the optical absorption coefficient. In particular, the sample with DZ structure becomes completely opaque above 16 GPa (see Fig. 10); thus, suggesting that the sample has undergone a PT to the same octahedrally-coordinated DR structure with metallic character previously observed during the first upstroke of the DS phase above 18 GPa.

4.4. Second downstroke

Finally, to verify the reversibility of the DZ-to-DR PT, we have performed a study of the DZ sample on decreasing pressure to 1 atm. At this pressure, the DZ sample recovers again the transmittance in the visible range below 5 GPa (see Fig. 10), thus showing the same aspect as before the second upstroke. Therefore, we can conclude that the DZ-to-DR PT in ZnGa$_2$Se$_4$ is completely reversible, as it has been observed in CdGa$_2$Se$_4$ [18]. The reversibility of the DZ-to-DR PT can be understood since both phases show a complete disorder of cations and vacancies at the cation sites, as already commented. The change is the cation coordination: from 4 in the DZ phase to 6 in the DR phase. Therefore, the DZ-to-DR PT is reversible since no order-disorder process is involved.

5. Conclusions

We have reported optical absorption measurements under pressure in DC- and DS- ZnGa$_2$Se$_4$ up to 22 GPa. This has allowed us to study the pressure dependence of the optical absorption edge of an OVC with DS structure (not previously done to our knowledge) and compare the pressure dependence of the optical absorption edge of two different phases of the same compound and how pressure-induced order-disorder processes affect both phases. Our measurements show that the direct bandgap energy of the DC sample is slightly larger (0.1 eV) than that of the DS sample and that both samples undergo similar changes under compression. In particular, the direct bandgap energy of both DC- and DS-ZnGa$_2$Se$_4$ shows a strong non-linear pressure dependence in good agreement with previous optical absorption measurements in other adamantine OVCs under compression. Therefore, this work shows for

the first time that also an OVC with the DS structure exhibits the strong non-linear pressure dependence previously found in OVCs with DC structure as well as in monoclinic Ga_2S_3 and Ga_2Se_3. Thanks to theoretical calculations in DC-$ZnGa_2Se_4$, the strong non-linear pressure dependence of the direct bandgap energy in DC-$ZnGa_2Se_4$ has been attributed to: i) the band anticrossing occurring between the two lowermost conduction bands, as previously observed in other OVCs, including DC-$CdGa_2S_4$, DC-$HgGa_2S_4$, DC-$CdGa_2Se_4$, and DC-$HgGa_2Se_4$; and ii) the strong pressure coefficient of the valence band maximum at all pressures (only slightly smaller than that of the conduction band minimum at low pressure up to around 10 GPa). In this work, we conclude that the same mechanism allows to explain the strong non-linear pressure dependence of the direct bandgap energy in DS-$ZnGa_2Se_4$, and by extension could be valid for all DS phases of AB_2X_4 OVCs. Consequently, this work allows completing the demonstration that the non-linear pressure dependence of the direct bandgap is common to all OVCs with ordered or slightly disordered structures, like the DC and DS structures, as already hypothesized twelve years ago [27].

At pressures beyond 10 GPa, a strong decrease of the experimental bandgap energy was found in both DC and DS samples. The decrease of the experimental bandgap energy in DC-$ZnGa_2Se_4$ is found to be larger than that attributed to the theoretical bandgap energy. Therefore, the larger decrease of the experimental bandgap above 10 GPa than theoretically expected is attributed to the increase of pressure-induced disorder in the sample since the disorder effect is not included in our calculations. The pressure-induced disorder at cation sites leads to a progressive PT from the DC structure to the DS structure, afterwards to the DCA structure, and finally to the disordered rocksalt DR structure. For DC-$ZnGa_2Se_4$, the disorder conducing to the DS phase starts above 10 GPa and the final transition to the DR phase occurs above 25 GPa. For DS-$ZnGa_2Se_4$, a similar scenario occurs, with the disorder conducing to the DCA phase starting above 10 GPa, and the final transition to the DR phase occurring above 20 GPa.

On decreasing pressure from 22 GPa, where samples are opaque due to the metallic character of the high-pressure DR phase, we have found that the recovered samples become transparent below 5 GPa. However, the direct bandgap of the recovered samples is much smaller (0.35 eV) than those of the initial DC and DS phases, being the bandgap of the sample recovered from the DS sample smaller (0.1 eV) than that of the sample recovered from the DC sample. We have interpreted these results as evidence that DCA and DZ phases are formed on decreasing pressure (from 22 GPa) from original DC and DS phases, respectively, due to the irreversibility of the pressure-induced disorder process. With these results, we also show for the first time that on decreasing pressure from the same pressure, different disordered phases are formed in OVCs depending on the cation disorder already present in the original samples. We have explained that the decrease of the direct bandgap energy with increasing disorder in adamantine OVCs can be attributed to the larger average cation-anion distance in the more disordered phases, which is reflected in their larger volumes per formula unit.

We have additionally measured the pressure dependence of the optical absorption edge of the recovered DCA- and DZ-$ZnGa_2Se_4$ phases on increasing pressure up to 8 GPa (during a second upstroke) and determined the pressure coefficients of their direct bandgap energies. These values have been compared to those previously found in other disordered phases of adamantine OVCs and has been proved that the pressure coefficient of the direct bandgap energy decreases on increasing the disorder degree in $ZnGa_2Se_4$; a result which is in good agreement with previous measurements on disordered samples of $HgGa_2Se_4$. Finally, we have explained that the decrease of the pressure coefficient of the direct bandgap energy with increasing disorder in adamantine OVCs can be explained by the nature of the lowermost CB in disordered phases. This CB is

considered a mixture of both lowermost CBs of the fully ordered DC structure. The higher the disorder the larger the mixture of both bands and the smaller the pressure coefficient of the direct bandgap energy.

We hope the present study will help to distinguish between the optical properties of DC, DS, DCA, and DZ phases of $ZnGa_2Se_4$ at room conditions and promote the study and applications of adamantine AB_2X_4 OVCs. In particular, this work will open the door to studies of photoelastic and photoconductive properties in adamantine OVCs that are expected to be more tunable than those observed in binary zincblende and wurtzite semiconductors (ZnO, ZnS, ZnSe, and CdS). Now that the operating mechanism of the photoelastic and photoconductive properties related to vacancies and other undesired defects in binary tetrahedrally-coordinated compounds is better understood, it is timely to explore the richer behavior of ternary tetrahedrally-coordinated compounds, like adamantine OVCs, that intrinsically incorporate vacancies in their crystalline structures.

CRediT authorship contribution statement

O. Gomis: Conceptualization, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Supervision. **R. Vilaplana**: Investigation, Writing – review & editing. **E. Pérez-González**: Formal analysis. **J. Ruiz-Fuertes**: Investigation, Formal analysis. **P. Rodríguez-Hernández**: Formal analysis. **A. Muñoz**: Formal analysis. **D. Errandonea**: Investigation, Writing – review & editing. **A. Segura**: Investigation, Writing – review & editing. **D. Santamaría-Pérez**: Investigation, Writing – review & editing. **P. Alonso-Gutiérrez**: Resources, Investigation. **M. L. Sanjuan**: Resources, Investigation, Writing – review & editing. **I. M. Tiginyanu**: Resources, Investigation. **V. V. Ursaki**: Resources, Investigation. **F. J. Manjón**: Conceptualization, Validation, Investigation, Writing – original draft, Writing – review & editing, Funding acquisition.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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