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$HgGa_2Se_4$ under high pressure: An optical absorption study

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High-pressure optical absorption measurements have been performed in defect chalcopyrite $HgGa_2Se_4$ to investigate the influence of pressure on the bandgap energy and its relation with the pressure-induced order–disorder processes that occur in this ordered-vacancy compound. Two different experiments have been carried out in which the sample undergoes either a partial or a total pressure-induced disorder process at 15.4 and 30.8 GPa, respectively. It has been found that the direct bandgap energies of the recovered samples at 1 GPa were around 0.15 and 0.23 eV smaller than that of the original sample, respectively, and that both recovered samples have different pressure coefficients of the direct bandgap than the original sample. A comprehensive explanation for these results on the basis of pressure-induced order–disorder processes is provided.

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1 Introduction $HgGa_2Se_4$ is an adamantine-type $A^{II}B_2^{III}X_4^{VI}$ ordered-vacancy compound (OVC) which crystallizes in the tetragonal defect chalcopyrite (DC) structure whose space group (S.G.) is I-4, No. 82. A feature of OVCs is that they are tetrahedrally coordinated semiconductors that have a vacant cationic site in an ordered and stoichiometric fashion, i.e., a stoichiometric vacancy located at a fixed Wyckoff position in the unit cell [1]. The presence of a stoichiometric vacancy in the unit cell leads to a more complex physics in OVCs than in common semiconductors and explains why OVCs have been less studied than common binary and ternary chalcogenide semiconductors.

OVCs are interesting compounds to study the order–disorder phase transitions occurring in tetrahedrally coordinated semiconductors and the influence of cation disorder in the physicochemical properties of semiconductors. A common trend in all adamantine OVCs is that they have several non-equivalent tetrahedrally coordinated cations and a vacancy in the unit cell which results in a distortion of the crystal lattice from the cubic symmetry. The lack of cubic symmetry of OVCs, their anisotropy, and their wide range of bandgap energies provide special properties to this family of semiconductors with important technological applications in optoelectronics, solar cells, and non-linear optics that have been the subject of several reviews [1–4].

High-pressure studies of OVCs with $A^{II}B_2^{III}X_4^{VI}$ stoichiometry are receiving increasing attention in the last years [5–36]. The vast majority of these works have been focused on the study of the structural and vibrational properties of $A^{II}B_2^{III}X_4^{VI}$ compounds by means of X-ray diffraction (XRD) and Raman scattering (RS)

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measurements, respectively. In particular, three high-pressure works have recently reported the structural and vibrational properties of DC-$HgGa_2Se_4$ under pressure where pressure-induced phase transitions have been observed [24, 25, 28]. The disordered stannite (DS) structure and the disordered rocksalt (DR) structure have been proposed as the high-pressure phases of DC-$HgGa_2Se_4$ [24, 25, 28]. In addition, the DR phase of $HgGa_2Se_4$ on downstroke undergoes a phase transition below 2.1 GPa to a phase assigned to a disordered zincblende (DZ) structure [24, 28]. However, to the best of our knowledge, only three works have been devoted to the experimental high-pressure study of the optical absorption of the OVC family [6, 21, 23]. In this respect, the pressure dependence of the direct bandgap energy of semimagnetic $MnGa_2Se_4$ [6], and of DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$ [21] was reported. This last work was focused on the explanation of the strong non-linear pressure dependence of the direct bandgap energy in both compounds at relatively low pressures. Finally, a comprehensive work showing the correlation of RS and optical absorption measurements on DC-$CdGa_2Se_4$ was reported in Ref. [23], where the effects of the pressure-induced order–disorder processes occurring in OVCs were addressed.

In order to improve the knowledge of the high-pressure behavior of AGa_2Se_4 (A = Zn, Cd, Hg) compounds, we report in this work an optical absorption study of DC-$HgGa_2Se_4$, which has been studied in two runs up to pressures of 15.4 and 30.8 GPa, respectively. As it has been commented, a partial report of our results has been already published [21]. In this work, we demonstrate that the maximum pressure reached in the experiments is important in order to shed light on the complex pressure-induced order–disorder processes occurring in OVCs and to understand the relationship between structure and optical properties in the recovered samples of these defective compounds.

2 Experimental Single crystals of DC-$HgGa_2Se_4$ with around 20 μm in thickness were grown from its constituents HgSe and Ga_2Se_3 by chemical vapor transport method using iodine as a transport agent [37]. The as-grown crystals represent triangular prisms with mirror-like surfaces. Chemical and structural analyses have shown the stoichiometric composition of the crystals and no spurious phases were observed. Ambient pressure XRD and RS measurements previously published confirmed that our sample has a DC-type structure [24, 28].

High-pressure optical absorption experiments at room temperature were performed by the sample-in sample-out method using a micro-optical system [38] in combination with a tungsten lamp and an Ocean Optics spectrometer. Samples were loaded in a membrane-type diamond anvil cell together with a 16:3:1 methanol–ethanol–water mixture as pressure-transmitting medium and ruby grains for pressure calibration with the ruby fluorescence method [39]. Stray light was measured in the high absorption region of the sample for every spectrum and subtracted from the transmission spectrum. Afterwards, the experimental transmittance spectrum was scaled in order to fit the theoretical value of the transmittance in the spectral range through which the sample is transparent (absorption coefficient $\alpha = 0$). The value used for the theoretical transmittance T_{teor} is given by the following equation [40]:

$$T_{teor} = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}, \quad (1)$$

where R is the reflectance, α the absorption coefficient, and d the sample thickness. The reflectance is given by the following equation [40]:

$$R = \left[\frac{n - n_0}{n + n_0}\right]^2, \quad (2)$$

where n is the refractive index of the sample and n_0 the refractive index of the methanol–ethanol–water pressure transmitting medium. In this way, the scaling procedure gives a corrected experimental transmittance T given by $T = cT_{teor}$ being c the correction factor.

Finally, the absorption coefficient α was obtained from the corrected experimental transmittance T taking into account Eq. (1) by

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

In our particular case for DC-$HgGa_2Se_4$, we have taken $d = 20$ μm, $n = 2.6$ [41], and $n_0 = 1.35$ [42].

The study of 20-μm-thick samples allows to get relatively small values of α which enables one to explore both indirect and direct bandgaps; however, they prevent a precise determination of the direct bandgap by fitting the optical absorption edge [43, 44]. In this respect, we have obtained the direct bandgap by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ vs. $h\nu$ plot to zero absorption. This method has yielded rather accurate values of the pressure coefficient of the direct bandgap energy and only slightly underestimated values of the direct bandgap as commented in Refs. [21, 23] for both DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$. For DC-$HgGa_2Se_4$, we obtained an experimental direct bandgap of 1.93 eV at room pressure [21], which is very close to the accepted value between 1.95 and 1.99 eV [45, 46].

In this work, we report results of two optical absorption experiments at high pressures that allow us to study the pressure dependence of the bandgap energy in DC-$HgGa_2Se_4$ and in recovered samples of $HgGa_2Se_4$ obtained after reaching different pressures on upstroke. The two experiments consisted of two consecutive upstrokes and downstrokes and allowed us to study the reversibility of the pressure-induced order–disorder processes which lead from the initial ordered DC phase to high-pressure phases with

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partial or total cation–vacancy disorder [24, 28]. In the first experiment, partially reported in Ref. [21], we increased pressure only up to 15.4 GPa in order to induce a partial cation–vacancy disorder in the samples since at this pressure the sample has not undergone a complete phase transition to the DR phase [24, 28]. In the second experiment, we increased pressure up to 30.8 GPa in order to induce a total cation–vacancy disorder, transforming our sample to the opaque DR structure, as shown in previous high-pressure XRD and RS measurements in DC-$HgGa_2Se_4$ [24, 28]. In both experiments, pressure was slowly decreased to 1.0 GPa after the first upstroke in order to study the reversibility of the defects created during the first upstroke and its effect on the bandgap energy. In summary, the main difference between both experiments is the maximum pressure reached (15.4 and 30.8 GPa) which influences the completion of the phase transition to the opaque DR phase observed in previous experiments above 17–22 GPa depending on the technique used and the hydrostatic conditions of the experiment [24, 28]. We will show that the study of the optical absorption of the recovered samples from both experiments shows important differences in order to understand pressure-induced order–disorder processes in OVCs.

3 Results and discussion

Our aim is to show that high-pressure optical absorption measurements on DC-$HgGa_2Se_4$ evidence changes in the optical properties that correlate with changes in the structural and vibrational properties already seen in previous high-pressure XRD and RS experiments carried out under similar conditions [24, 25, 28]. Therefore, hereafter we will explain the results of our high-pressure optical absorption experiments by correlating them with the different phases of $HgGa_2Se_4$ discussed in previous works (DC, DS, DR and DZ).

Figure 1 shows a selection of the optical absorption spectra in DC-$HgGa_2Se_4$ during the first upstroke up to 15.4 GPa. As it can be observed, there is a blue shift of the fundamental absorption edge with increasing pressure up to 11.2 GPa and a red shift between this pressure and 15.4 GPa. At pressures higher than 14.8 GPa, the presence of a great number of dark linear defects in the sample results in an almost complete darkening of the samples and a very large low-energy tail in the absorption spectra due to light absorption by defects. Therefore, the estimation of the direct bandgap energy has not been possible above 14.8 GPa.

As commented in a previous work, a low-energy tail begins to appear in the optical absorption spectrum of DC-$HgGa_2Se_4$ around 11.8 GPa [21]. The appearance of a low-energy tail in the optical absorption spectrum of a direct bandgap semiconductor could be attributed to the observation of an indirect bandgap below the direct bandgap due to a direct-to-indirect bandgap crossover [43, 44, 47] or to the optical absorption by defects which are precursors of a phase transition [44, 48, 49]. In this respect, *ab initio* calculations for DC-$HgGa_2Se_4$ reported in Ref. [21] concluded that the bandgap is of direct type and that a direct-to-indirect

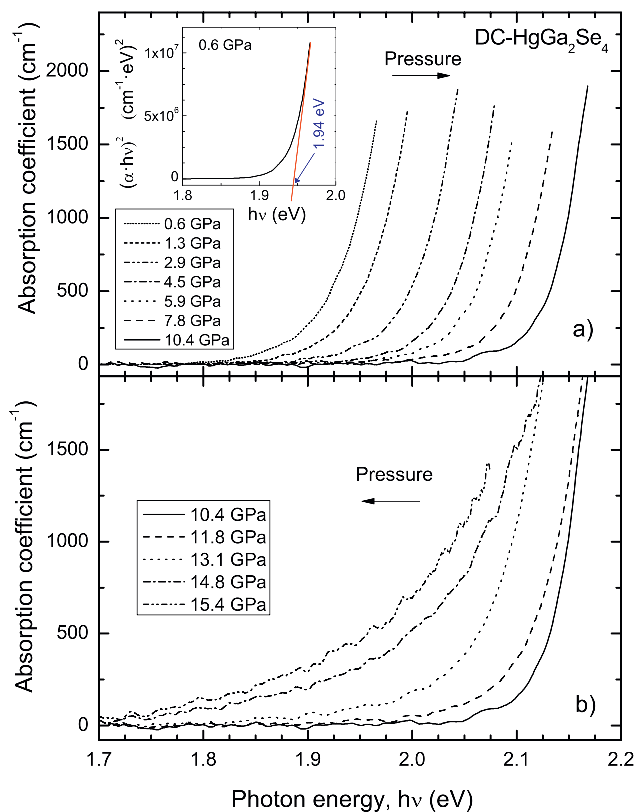

Figure 1 Optical absorption edge of DC-$HgGa_2Se_4$ on increasing pressure up to 10.4 GPa (a) and from 10.4 up to 15.4 GPa (b). Inset shows a plot of $(\alpha h\nu)^2$ vs. $h\nu$ where the tangent method is applied to estimate the direct bandgap energy of DC-$HgGa_2Se_4$ from the absorption coefficient at 0.6 GPa in the first upstroke.

bandgap crossover would only occur at pressures higher than 16 GPa, i.e., at pressures at which the bandgap cannot be estimated experimentally because of the light absorption by defects. Therefore, the appearance of the low-energy tail observed between 12 and 16 GPa in $HgGa_2Se_4$ cannot be attributed to the indirect bandgap. This situation is similar to that of DC-$CdGa_2Se_4$ above 6–8 GPa [23].

Figure 2 shows images taken during the second experiment up to 30.8 GPa. It can be observed that the original DC-$HgGa_2Se_4$ sample presents a reddish color at 0.6 GPa and that on increasing pressure to 11.8 GPa the sample becomes more transparent. Above this pressure, dark linear defects, which are precursors of a phase transition, appear together with the appearance of the low-energy tail. At 30.8 GPa, the sample appears black in color because of the completion of the phase transition to the opaque DR phase.

Figure 3 shows the pressure dependence of the direct bandgap energy (circles) in DC-$HgGa_2Se_4$ during the first upstroke which is estimated by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ vs. $h\nu$ plot to zero absorption. Inset of Fig. 1 shows a plot of $(\alpha h\nu)^2$ vs. $h\nu$ where the tangent method is applied to estimate the direct bandgap energy of DC-$HgGa_2Se_4$ from the absorption coefficient at 0.6 GPa in the first upstroke. Error bars for the

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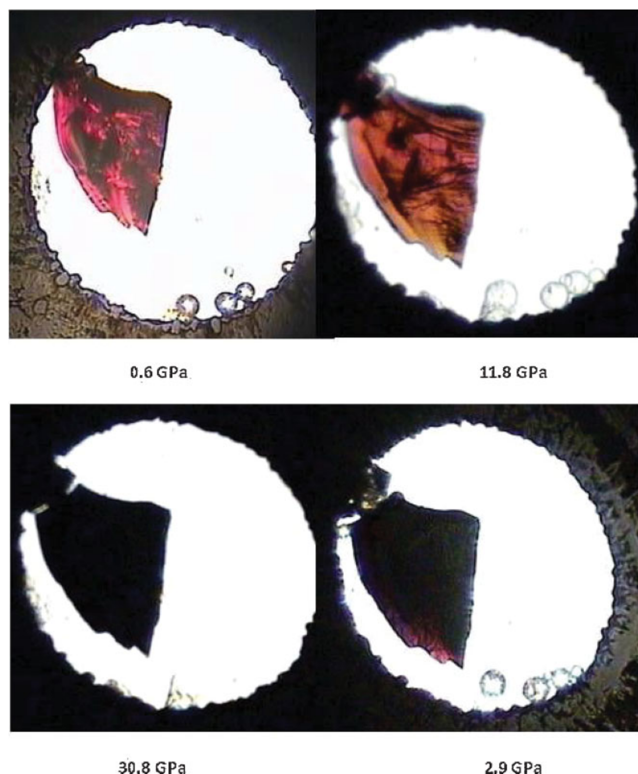

Figure 2 Sequence of photographs of the $HgGa_2Se_4$ crystal taken during the first upstroke of the second experiment at 0.6, 11.8, and 30.8 GPa. The last photograph was taken at 2.9 GPa during the second upstroke of the second experiment.

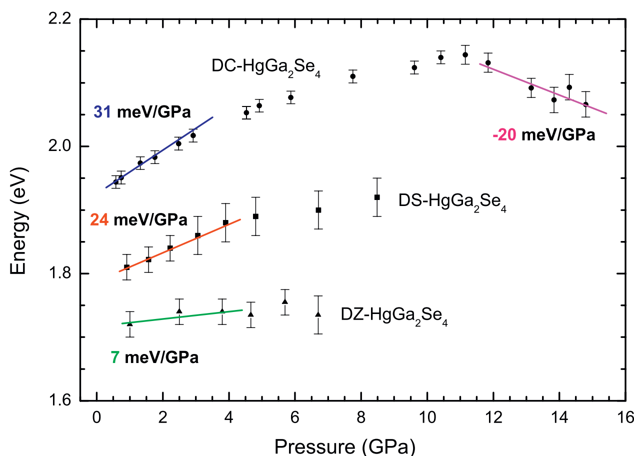

Figure 3 Pressure dependence of the bandgap energy in the different phases of $HgGa_2Se_4$. Circles with error bars are obtained during a first upstroke. Triangles with error bars, and squares with error bars are obtained during a second upstroke in recovered DZ and DS samples after increasing pressure during a first upstroke up to 30.8 and 15.4 GPa, respectively. Experimental values of pressure coefficients of the direct bandgaps at low pressure (in the DC, DS, and DZ phases) and at high pressure (in the DC phase) are also shown. Colored solid lines are just guides to the eye for establishing the slopes of the bandgaps in the different structures of $HgGa_2Se_4$ and are not related to any kind of phase transition in this compound.

bandgap energies have been estimated by taking into account the different ranges of absorption coefficient values for which the relationship $(\alpha h\nu)^2$ vs. $h\nu$ is linear at each different pressure. These different ranges of the absorption coefficient values give different values of the bandgap energy depending on the slope of the straight line obtained from the linear fit. Note that the error bar for the bandgap energy increases at pressures above 11.8 GPa due to the presence of the low-energy tail. In Fig. 3, it can be observed that the direct bandgap energy of DC-$HgGa_2Se_4$ exhibits a strong non-linear pressure dependence up to 8 GPa. This behavior was already observed in DC-$HgGa_2Se_4$ and also in DC-$CdGa_2Se_4$ and explained on the basis of theoretical *ab initio* calculations which demonstrated that this non-linear behavior is a general feature common to all OVCs [21]. In particular, it was proposed that this behavior was due to a conduction band anticrossing at the Γ point of the Brillouin zone caused by two factors: (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.

It can be observed that the direct bandgap energy in DC-$HgGa_2Se_4$ increases at low pressures with a pressure coefficient of 31 ±4 meV/GPa estimated from a linear fit in the range 0.6–2.9 GPa (see blue line in Fig. 3), while at pressures above 11.8 GPa the bandgap energy decreases with a pressure coefficient of −20 ±3 meV/GPa estimated from a linear fit in the range 11.8–14.8 GPa (see pink line in Fig. 3). We note that a rough estimate of the pressure coefficient of the direct bandgap can also be obtained by measuring the shift of the optical absorption edge at a constant high absorption coefficient. Following this procedure, the pressure coefficients obtained for the direct bandgap energy of DC-$HgGa_2Se_4$ at low pressure in the range 0.6–2.9 GPa and at high pressure in the range 11.8–14.8 GPa are 31 ± 1 and −20 ± 6 meV/GPa, respectively, which agree with those previously obtained from the linear extrapolation method. A similar behavior was observed in DC-$CdGa_2Se_4$ [21, 23], and the gradual decrease of its direct bandgap above 6–8 GPa was interpreted as a signature of the onset of the cation disorder process that gradually transforms the DC phase to a structure with a partial disorder which was tentatively attributed to a DS structure [23].

We must note that a change in the sign of the pressure coefficient of the direct bandgap above certain pressure was already noted in some chalcopyrites, like $CuAlSe_2$ [50], and in defect zincblende compounds, like Ga_2Se_3 [51]. In these works, the change of sign of the pressure coefficient was attributed either to a direct–pseudodirect bandgap crossover [50] or to a direct–indirect bandgap crossover [51]. In this respect, we have discarded these two interpretations, as has been previously commented, because we have performed band structure calculations in DC-$HgGa_2Se_4$ (see Ref. [21])

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and our calculations do not support the direct–indirect bandgap crossover as the origin of the decrease of the bandgap above 11.2 GPa in DC-$HgGa_2Se_4$. Moreover, we must note that in DC-$HgGa_2Se_4$ the appearance of a low-energy tail in the optical absorption spectrum begins around 12 GPa which is coincident with the onset of a stronger decrease of the bandgap energy as in DC-$CdGa_2Se_4$ [23]. Therefore, we may attribute both the abrupt decrease of the bandgap energy in DC-$HgGa_2Se_4$ and the appearance of the low-energy tail around 12 GPa to the onset of the cation–cation or cation–vacancy disorder processes. This process gradually transforms the initial DC phase of $HgGa_2Se_4$ first to a structure with partial cation disorder, tentatively attributed to a DS phase [28], and then at higher pressures to a structure with full cation–vacancy disorder and considered to be the DR phase [24, 28].

As it was previously mentioned, we have performed two optical absorption experiments up to different maximum pressures in order to obtain information on the reversibility of the order–disorder processes associated to the DC→DR phase transition. In the experiment up to 15.4 GPa, the sample was partially opaque due to the appearance of dark linear defects above 12 GPa. In the experiment up to 30.8 GPa, the sample became completely opaque above the phase transition to the DR phase and during the pressure release we found that the opaque sample recovered its transparency below 5 GPa. We must stress that in both experiments, the recovered samples at 1.0 GPa on downstroke showed dark linear defects that were not present in the original DC samples and that the direct bandgap energy at 1.0 GPa after dowstroke was smaller in both samples than in the initial DC samples at a similar pressure upon upstroke. In particular, the samples recovered from 15.4 and 30.8 GPa showed a direct bandgap energy that was around 0.15 and 0.23 eV smaller than that measured at the same pressure in the original DC phase, respectively (see squares and triangles in Fig. 3). To clarify this issue, Fig. 2 shows an image of the sample at 2.9 GPa obtained during a second upstroke after decreasing slowly pressure down to 1 GPa from 30.8 GPa. As it can be observed, the sample retains some dark linear defects from the transition to the DR phase and has a dark red color that evidences the decrease of the bandgap energy with respect to the image of the original sample at 0.6 GPa. A similar phenomenon is observed in the sample compressed only to 15.4 GPa. These results indicate that dark linear defects are not reversible and the change of the bandgap energy above 12 GPa (once dark linear defects appear) is also not reversible. The decrease of the bandgap energy observed in DC-$HgGa_2Se_4$ above 12 GPa, that we have attributed to increasing disorder, is similar to that observed in chalcopyrites [52] and in other ternary OVCs, like $CdGa_2Te_4$ [3], $CdGa_2Se_4$ [23], $HgGa_2S_4$ [26], and $ZnGa_2Se_4$ [27, 30]. We want to stress that the irreversibility of the direct bandgap energy and its decrease in value in the recovered samples of OVCs can be explained by the irreversible cation–cation and cation–vacancy order–disorder processes which may result in different recovered structures from that of the original phase. Those recovered structures depend on the maximum pressure attained by the sample in the original phase.

In the following paragraph, we will discuss about the possible structures of the recovered samples in $HgGa_2Se_4$ on the basis of our present results of high-pressure optical absorption measurements and of previous results of high-pressure XRD and RS measurements [24, 28]. Regarding the nature of the samples recovered from 30.8 GPa, we must recall that the presence of DZ-$HgGa_2Se_4$ on downstroke after the transformation of DC-$HgGa_2Se_4$ to the DR structure has been evidenced by XRD and RS measurements [24, 28]. Furthermore, a decrease of the direct bandgap energy by 0.4 eV was already observed in a recovered sample with DZ structure in $CdGa_2Se_4$ obtained after transforming DC-$CdGa_2Se_4$ to the DR structure above 20 GPa [23]. Therefore, we tentatively attribute the sample recovered at 1.0 GPa from 30.8 GPa, which shows a direct bandgap 0.23 eV smaller than the DC phase, to DZ-$HgGa_2Se_4$.

With regard to the nature of the sample recovered from 15.4 GPa, it is known that $ZnGa_2Se_4$ samples with partial cation or cation–vacancy disorder, like those crystallizing in the DS structure, show a slightly smaller bandgap energy than ordered samples with the DC structure [30]. Therefore, the smaller decrease of the direct bandgap in the sample recovered from 15.4 GPa than that recovered from 30.8 GPa prompts to attribute it to a structure with an intermediate degree of disorder between that of DC and DZ structures. In this respect, different intermediate structures between these two structures have been recently discussed [53]. In particular, a phase with a possible DS structure (likely model 7 of Ref. [53] where cations and vacancies become partially mixed) was found in RS measurements of DC-$HgGa_2Se_4$ above 19 GPa [28]. This DS phase shows more Raman peaks than the DC phase because of the partial occupation of the vacancy position [28]. However, the disappearance of the A_2 Raman mode (characteristic of the DC structure) above 14.5 GPa in $HgGa_2Se_4$ [28] suggests that a DS phase is already formed at this pressure. This phase obtained after compressing DC-$HgGa_2Se_4$ above 14.5 GPa seems to be different from the DS phase found previously above 19 GPa since no new Raman modes are present between 14.5 and 19 GPa [28]. The DS phase of $HgGa_2Se_4$ above 14.5 GPa is likely to be similar to that already observed in $CdGa_2Se_4$ (model 2 or 6 of Ref. [53] where cations and vacancies are not mixed) [23]. Since the onset of structural disorder in $HgGa_2Se_4$ is observed above 12 GPa, we consider that pressures above 12–13 GPa are high enough to observe the irreversibility of the pressure-induced disorder process in DC-$HgGa_2Se_4$. Consequently, hereafter we will consider that the sample obtained after pressurization of DC-$HgGa_2Se_4$ to 15.4 GPa is a partially disordered DS structure likely corresponding to model 2 or 6 of Ref. [53].

Figure 4 shows selected optical absorption spectra at high pressures of the samples with DS and DZ structures recovered from 15.4 GPa and from 30.8 GPa, respectively.

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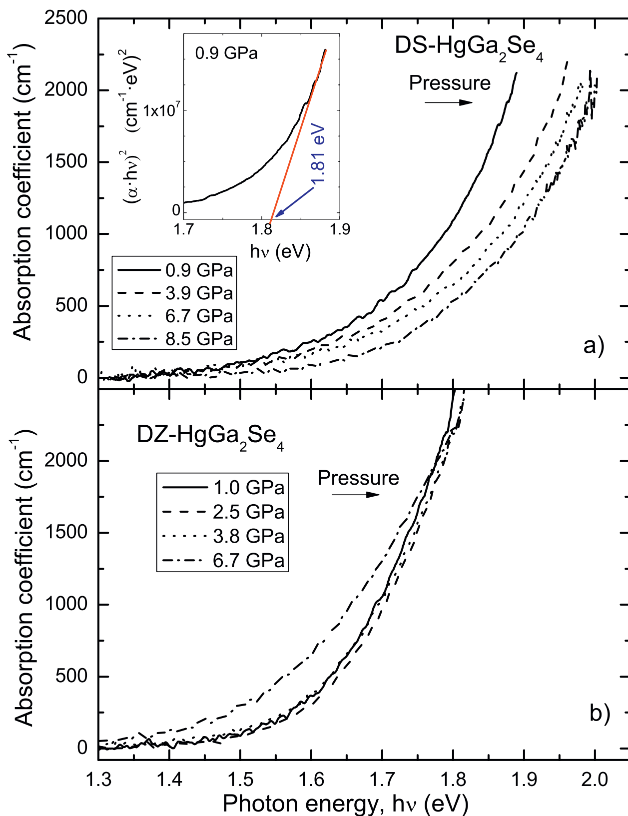

Figure 4 Pressure dependence of the optical absorption edge of the recovered samples of $HgGa_2Se_4$ measured during a second upstroke in the first (a) and second (b) experiment, i.e., after having increased pressure in the first upstroke up to 15.4 GPa and up to 30.8 GPa, respectively. Inset shows a plot of $(\alpha h\nu)^2$ vs. $h\nu$ where the tangent method is applied to estimate the direct bandgap energy of DS-$HgGa_2Se_4$ from the absorption coefficient at 0.9 GPa in the second upstroke.

These measurements were obtained during a second upstroke after recovering the samples to pressures near 1 GPa. In both recovered samples, the optical absorption edge exhibits a blue shift with increasing pressure more pronounced for the case of the DS phase. DS and DZ samples exhibit a progressive darkening above 6–8 GPa that prevents a good measurement of the optical absorption spectrum at higher pressures. In fact, a complete darkening of the DS and DZ samples was observed around 14 GPa. This last pressure is in agreement with the pressure (16 GPa) at which RS measurements, performed during a second upstroke in a DZ-$HgGa_2Se_4$ sample recovered from the DR phase, showed no Raman activity as expected after the transition to the DR phase [28]. Therefore, on the basis of these results, we tentatively attribute the high-pressure structure of the DS and DZ phases, found at pressures above those in which we observe the complete darkening of the samples, to the same octahedrally coordinated DR structure previously observed upon compression of the DC phase during the first upstroke [24, 28]. It must be stressed that the smaller pressure for the DS→DR and DZ→DR phase transitions than for the DC→DR phase transition is in good agreement with the order–disorder mechanism of the transitions from the DC, DS, and DZ phases to the completely disordered DR phase, i.e., the larger the disorder in the initial sample the smaller the phase transition pressure to the fully disordered high-pressure structure.

From the optical absorption measurements performed in the two recovered samples at different pressures, we have estimated the direct bandgap energy of the samples with DS and DZ structures 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. Inset of Fig. 4 shows a plot of $(\alpha h\nu)^2$ vs. $h\nu$ where the tangent method is applied to estimate the direct bandgap energy of DS-$HgGa_2Se_4$ from the absorption coefficient at 0.9 GPa in the second upstroke. The results for the direct bandgap energy of the DS and DZ phases up to 6–8 GPa are shown in Fig. 3 with squares and triangles, respectively. Note that theoretical calculations support the existence of a direct bandgap at smaller energy than the indirect bandgap in all OVCs (including those with DS and pseudocubic structures) at ambient pressure [21] and the same feature is expected for the DZ phase, as it occurs in most binary zincblende-type compounds [54]. The experimental pressure coefficient of the direct bandgap energy of DZ-$HgGa_2Se_4$ at low pressure has been estimated from a linear fit in the range 1.0–3.8 GPa to be around 7 ± 3 meV/GPa while the pressure coefficient at low pressure of the direct bandgap energy of the DS sample recovered from 15.4 GPa has been estimated from a linear fit in the range 0.9–3.9 GPa to be around 24 ± 6 meV/GPa. As it has been previously commented, we have also obtained the pressure coefficient of the direct bandgap energy by measuring the shift of the optical absorption edge at a constant high absorption coefficient. Following this procedure, the pressure coefficients obtained for the direct bandgap energy of the DZ and DS phases of $HgGa_2Se_4$ at low pressure in the ranges 1.0–3.8 and 0.9–3.9 GPa are 6 ± 3 and 22 ± 2 meV/GPa, respectively; which are in good agreement with those obtained with the linear extrapolation method. Both pressure coefficients for the recovered phases are smaller than that of the DC phase at low pressure (31 ± 4 meV/GPa), and much smaller than the pressure coefficients at low pressure of binary zincblende-type compounds, in particular ZnSe (70 meV/GPa [55, 56]) and HgSe (43 meV/GPa [56, 57]). Therefore, our results show that there is a clear decrease of the direct bandgap energy and its pressure coefficient with increasing disorder in OVCs. In the following paragraph, we will try to explain the reason for these two features of disordered phases in OVCs.

In order to address the explanation of the above-mentioned features, we have to consider the parallelism between the properties of ternary ABX_2 chalcopyrites and AB_2X_4 OVCs since both families of tetragonal compounds derive from the cubic zincblende structure. In these two tetragonal families, the different values of the bandgap energy of compounds with the same composition but different structures could be determined by three main

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factors: (i) tetragonal distortion of the crystal lattice, as described by the deviation of the axial *c/a* ratio from 2 (external distortion); (ii) displacement of anions from the ideal position in the zincblende structure (internal distortion); and (iii) cation–cation disorder (in chalcopyrites) and cation–cation or cation–vacancy disorder (in OVCs) [2]. It is well known that increasing disorder in chalcopyrites leads to the DZ structure with a smaller bandgap energy than that of the chalcopyrite structure [50, 52, 58]. On the other hand, it has been commented that increasing disorder in chalcopyrites leads to a negligible increase of the unit cell volume through a decrease of the tetragonal distortion (external distortion) and the tendency of anions on average toward the ideal position (internal distortion) in the zincblende structure [59]. Therefore, the decrease in the bandgap energy of chalcopyrites with increasing disorder cannot be ascribed to either the internal or external distortion and must be mainly ascribed to cation–cation disorder. This argument can be also extrapolated to ternary AB_2X_4 OVCs since the theoretical direct bandgap energy in these OVCs is only slightly changed by the modified structural parameters on going from the DC structure toward the DZ structure [4]. In fact, the decrease of the bandgap in the disordered phases of OVCs is observed irrespective of the volume of the DZ and DC phases as measured from XRD measurements. Note that DZ-$CdGa_2Se_4$ has a larger volume than DC-$CdGa_2Se_4$ [10] while DZ-$HgGa_2Se_4$ has a smaller volume than DC-$HgGa_2Se_4$ [24]; however, both compounds show a smaller bandgap in the DZ phase than in the DC phase. Therefore, we should ascribe the change in the direct bandgap energy of different structures in ternary AB_2X_4 OVCs mainly to the effect of cation or cation–vacancy disorder in complete parallelism with chalcopyrite compounds.

On the basis of the previous considerations, we have come to the conclusion that the decrease of the bandgap energy with increasing disorder in ternary AB_2X_4 OVCs, like $CdGa_2Se_4$ and $HgGa_2Se_4$, can be explained in the same way as it was previously explained in chalcopyrites [59], i.e., by the level repulsion effect responsible for bandgap bowing in alloys [60, 61] and by the formation of donor and acceptor pairs which lead to donor-like and acceptor-like bands inside the parent bandgap of the ordered compound [59]. On one hand, a small disorder in OVCs, like that occurring when going from DC to DS phases, leads to a small decrease of the bandgap energy because of the small repulsion effect between levels and the presence of relatively shallow donor-like and acceptor-like levels inside the bandgap of the parent DC phase. On the other hand, a larger disorder in OVCs, like that occurring in the DZ phase with a total cation–vacancy disorder in cation sites of the zincblende phase, leads to a larger decrease of the bandgap energy because of the larger repulsion effect between levels and the presence of deep donor-like and acceptor-like levels inside the bandgap of the parent DC phase.

We will discuss now the values of the pressure coefficients of the direct bandgap in the DS and DZ phases. In order to explain the pressure coefficient of the direct bandgap energy in DS-$HgGa_2Se_4$, which is intermediate between those of the DC and DZ phases, we want to stress that the DS phase is a tetragonal OVC and has two lowermost conduction bands, like the DC phase [21]. The smaller pressure coefficient of the direct bandgap energy in the DS phase with respect to the DC phase can be explained by considering that the bandgap energy of the DS phase is determined by the bands formed by shallow donors and acceptors, which arise during the transition from the DC to the DS phase. These donor-like and acceptor-like bands should have similar pressure coefficients than the lowermost conduction and topmost valence band, respectively. Finally, one has to take into account that the lowermost conduction band in the DS phase is expected to have a larger proportion of Ga cations located at 2*a* sites than in the DC phase, which mainly contribute to the second conduction band of the DC phase [21]. Since the second conduction band of the DC phase has a smaller pressure coefficient than the first conduction band [21], the disorder of Hg cations at 2*d* sites and Ga cations at 2*a* sites, as it would occur in model 2 of the DS phase in Ref. [53], would result in a larger contribution of Ga(2*a*) atoms to the lowermost conduction band than in the DC phase and consequently this would yield a smaller pressure coefficient of the direct bandgap energy in the DS phase than in the DC phase. In this sense, it must be stressed that model 6 of DS phase (in which Hg at 2*d* sites and Ga at 2*c* sites, i.e., located at the same cation plane perpendicular to the *c* axis, get mixed) is expected to have roughly the same pressure coefficient than the DC phase since both Hg(2*d*) and Ga(2*c*) atoms mainly contribute to the lowermost conduction band [21]. Therefore, our optical absorption measurements lead us to consider that the DS phase recovered in $HgGa_2Se_4$ from 15.4 GPa likely corresponds to model 2 of Ref. [53] where some Hg(2*d*) atoms occupy Ga(2*a*) positions at the same plane as vacancies (located at 2*b* Wyckoff sites).

Finally, the much smaller pressure coefficient of the bandgap energy in the DZ phase compared to the parent DC phase can be explained by the presence of deep acceptors and donors in the DZ phase. It is known that deep levels inside the bandgap (either with donor or acceptor character) have a very small pressure coefficient, owing to the nature of the localized close-range potential binding electrons, that is more determined by atomic electronegativity differences than by the crystal band structure [62, 63]. Therefore, the formation of deep donor-like and acceptor-like bands in the DZ phase reduce considerably both the bandgap energy and its pressure coefficient.

The above conclusion is supported by our theoretical calculations of the direct bandgap energy on $CdGa_2Se_4$ and $HgGa_2Se_4$ both in the DC (I-4) phase and in the ideal zincblende phase without disorder as performed in Ref. [4] (see Ref. [21] for theoretical details of our *ab initio* calculations). Note that the ideal zincblende phase was simulated for different volumes taking as basis a I-4 unit cell where the *c* parameter was fixed to $c = 2a$ and where the anion, located at the 8*g* Wyckoff position, was fixed at (1/4, 1/4, 1/8). In general, our calculations have confirmed the

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results of Ref. [4] and have shown that the pressure coefficient of the direct bandgap energy in the ideal zincblende phase without disorder, for both compounds, is twice the pressure coefficient in the DC phase. This result is in complete contradiction to our experimental results which show a considerable decrease of the pressure coefficient of the direct bandgap energy in the DZ phase with respect to the DC phase; therefore, we can conclude that the decrease of the pressure coefficient of the direct bandgap energy observed in the DZ phase must be mainly ascribed to the effect of disorder.

We want to clarify that the explanation we have provided in this work for the decrease of the direct bandgap energy and its pressure coefficient in the DZ phase of ternary AB_2X_4 OVCs is in contrast to that provided in a previous work related to DC-$CdGa_2Se_4$ [23]. In that work, it was considered that the smaller bandgap of the disordered DZ phase was mainly due to the larger unit cell volume of the DZ phase with respect to the DC phase and that the decrease of the pressure coefficient of the direct bandgap was due to the uneven mixture of the two lowermost conduction bands of the DC phase which contribute to the lowermost conduction band in the DZ phase. In this respect, we have to note that we have modified our view in this work on the light of the literature existing for ABX_2 compounds and the results which point to a negligible volume change with increasing disorder in ternary AB_2X_4 OVCs. In summary, we conclude that both the smaller direct bandgap energy and its smaller pressure coefficient in the DZ phase than in the DC phase can be explained by taking into account the deep acceptor-like and donor-like bands formed due to cation and cation–vacancy disorder present in the DZ phase of OVCs.

4 Conclusions

We have performed optical absorption measurements in tetragonal DC $HgGa_2Se_4$ (S.G. I-4) under high pressure. Two types of experiments performed in this OVC below and above 20 GPa have shown the importance of the maximum pressure applied to a DC sample in order to understand the effects of pressure-induced order–disorder processes on recovered samples. If applying pressure leads to a total cation–vacancy disorder, as in the cubic DR phase (S.G. Fm-3m), the sample usually returns on decompression to a cubic DZ structure (S.G. F-43m), also with total cation–vacancy disorder, showing the smallest direct bandgap and pressure coefficient. However, if pressure is not high enough to complete the phase transition to the DR phase the sample undergoes a partial cation–cation or cation–vacancy disorder and on decreasing slowly pressure the sample returns to a structure with a bandgap energy and pressure coefficient intermediate between those of the DC and DZ phases which we have attributed to a tetragonal DS (S.G. I-42m) phase (model 2 of Ref. [53]) in $HgGa_2Se_4$ pressurized to 15.4 GPa. The reason why the direct bandgap energy and its pressure coefficient for the disordered phases (DS and DZ) of OVCs are smaller than those inherent to the parent ordered DC phase has been explained by the level repulsion effect responsible for bandgap bowing in alloys and by the formation of donor and acceptor pairs in the DS and DZ phases which lead to donor-like and acceptor-like bands inside the parent bandgap of the ordered compound.

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