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Additional Information

HgGa₂Se₄ under high pressure: an optical absorption study

O. Gomis,^{1,*} R. Vilaplana,¹ F.J. Manjón,² J. Ruiz-Fuertes,^{3,4} E. Pérez-González,⁵ J. López-Solano,⁵ E. Bandiello,^{6,4} D. Errandonea,⁴ A. Segura⁴, P. Rodríguez-Hernández,⁵ A. Muñoz,⁵ V. V. Ursaki,⁷ and I. M. Tiginyanu⁷

¹*Centro de Tecnologías Físicas: Acústica, Materiales y Astrofísica, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain*

²*Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain*

³*Geowissenschaften, Goethe-Universität, Altenhöferallee 1, 60438 Frankfurt am Main, Germany*

⁴*Departamento de Física Aplicada-ICMUV, MALTA Consolider Team, Universidad de Valencia, Edificio de Investigación, C/Dr. Moliner 50, Burjassot, 46100 Valencia, Spain*

⁵*Departamento de Física, Instituto de Materiales y Nanotecnología, MALTA Consolider Team, Universidad de La Laguna, 38205 La Laguna, Tenerife, Spain*

⁶*Instituto de Ciencia Molecular, Universidad de Valencia, Paterna, 46980 Valencia, Spain*

⁷*Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, 2028 Chisinau, Moldova*

Abstract

High-pressure optical absorption measurements have been performed in defect chalcopyrite HgGa₂Se₄ 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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* Corresponding author, email: osgohi@fis.upv.es

41 1. Introduction

42 HgGa₂Se₄ is an adamantine-type $A^{II}B_2^{III}X_4^{VI}$ ordered-vacancy compound (OVC)
43 which crystallizes in the tetragonal defect-chalcopyrite (DC) structure whose space
44 group (S.G.) is *I*-4, No. 82. A feature of OVCs is that they are tetrahedrally-coordinated
45 semiconductors that have a vacant cationic site in an ordered and stoichiometric fashion;
46 i.e., a stoichiometric vacancy located at a fixed Wyckoff position in the unit cell [1].
47 The presence of a stoichiometric vacancy in the unit cell leads to a more complex
48 physics in OVCs than in common semiconductors and explains why OVCs have been
49 less studied than common binary and ternary chalcogenide semiconductors.

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

59 High-pressure studies of OVCs with $A^{II}B_2^{III}X_4^{VI}$ stoichiometry are receiving
60 increasing attention in the last years [5-36]. The vast majority of these works have been
61 focused on the study of the structural and vibrational properties of $A^{II}B_2^{III}X_4^{VI}$
62 compounds. In particular, three high-pressure works have recently reported the
63 structural and vibrational properties of DC-HgGa₂Se₄ under pressure where pressure-
64 induced phase transitions have been observed [24,25,28]. The disordered stannite (DS)
65 structure and the disordered rocksalt (DR) structure have been proposed as the high-
66 pressure phases of DC-HgGa₂Se₄ [24,25,28]. In addition, the DR phase of HgGa₂Se₄ on
67 downstroke undergoes a phase transition below 2.1 GPa to a phase assigned to a
68 disordered zincblende (DZ) structure [24,28]. However, to the best of our knowledge,
69 only three works have been devoted to the experimental high-pressure study of the
70 optical absorption of the OVC family [6, 21, 23]. In this respect, the pressure
71 dependence of the direct bandgap energy of semimagnetic MnGa₂Se₄ [6], and of DC-
72 CdGa₂Se₄ and DC-HgGa₂Se₄ [21] were reported. This last work was focused on the
73 explanation of the strong non-linear pressure dependence of the direct bandgap energy

74 in both compounds at relatively low pressures. Finally, a comprehensive work showing
75 the correlation of Raman scattering and optical absorption measurements on DC-
76 CdGa₂Se₄ was reported in **Ref. 23**, where the effects of the pressure-induced order-
77 disorder processes occurring in OVCs were addressed.

78 In order to improve the knowledge of the high-pressure behaviour of AGa₂Se₄
79 (*A*= Zn, Cd, Hg) compounds, we report in this work an optical absorption study of DC-
80 HgGa₂Se₄, which has been studied in two runs up to pressures of 15.4 and 30.8 GPa,
81 respectively. As it has been commented, a partial report of our results has been already
82 published [21]. In this work, we demonstrate that the maximum pressure reached in the
83 experiments is important in order to: i) shed light on the complex pressure-induced
84 order-disorder processes occurring in OVCs and ii) understand the relationship between
85 structure and optical properties in these defective compounds.

86

87 **2. Experimental section**

88 Single crystals of DC-HgGa₂Se₄ with around 20 μm in thickness were grown
89 from its constituents HgSe and Ga₂Se₃ by chemical vapor transport method using iodine
90 as a transport agent [37]. The as-grown crystals represent triangular prisms with mirror-
91 like surfaces. Chemical and structural analyses have shown the stoichiometric
92 composition of the crystals and no spurious phases were observed. Ambient pressure x-
93 ray diffraction (XRD) and Raman scattering (RS) measurements previously published
94 confirmed that our sample has a DC-type structure [24, 28].

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

106
$$T_{\text{teor}} = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad (1)$$

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

109
$$R = \left[\frac{n - n_0}{n + n_0} \right]^2 \quad (2)$$

110 where n is the refractive index of the sample and n_0 the refractive index of the methanol-
 111 ethanol-water pressure transmitting medium. In this way, the scaling procedure gives a
 112 corrected experimental transmittance T given by $T = c \cdot T_{\text{teor}}$ being c the correction factor.
 113 Finally, the absorption coefficient α was obtained from the corrected experimental
 114 transmittance T taking into account **Ec. (1)** by:

115
$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{2T} + \sqrt{\left[\frac{(1-R)^2}{2T} \right]^2 + R^2} \right] \quad (3)$$

116 In our particular case for DC-HgGa₂Se₄, we have taken $d = 20 \mu\text{m}$, $n = 2.6$ [41] and $n_0 =$
 117 1.35 [42].

118 The study of 20- μm -thick samples allows to get relatively small values of
 119 α which enables one to explore both indirect and direct bandgaps; however, they
 120 prevent a precise determination of the direct bandgap by fitting the optical absorption
 121 edge [43,44]. In this respect, we have obtained the direct bandgap by extrapolating the
 122 linear fit of the high-energy part of the $(\alpha \cdot \text{h}\nu)^2$ vs. $\text{h}\nu$ plot to zero absorption. This
 123 method has yielded rather accurate values of the pressure coefficient of the direct
 124 bandgap energy and only slightly underestimated values of the direct bandgap as
 125 commented in **Refs. 21** and **23** for both DC-CdGa₂Se₄ and DC-HgGa₂Se₄. For DC-
 126 HgGa₂Se₄, we obtained an experimental direct bandgap of 1.93 eV at room pressure
 127 [21], which is very close to the accepted value between 1.95 and 1.99 eV [45,46].

128 In this work, we report results of two optical absorption experiments at high
 129 pressures that allow us to study the pressure dependence of the bandgap energy in DC-
 130 HgGa₂Se₄ and in recovered samples of HgGa₂Se₄ obtained after reaching different
 131 pressures on upstroke. The two experiments consisted of two consecutive upstrokes and
 132 downstrokes and allowed us to study the reversibility of the pressure-induced order-
 133 disorder processes which lead from the initial ordered DC phase to high-pressure phases
 134 with partial or total cation-vacancy disorder [24,28]. In the first experiment, partially

135 reported in **Ref. 21**, we increased pressure only up to 15.4 GPa in order to induce a
136 partial cation-vacancy disorder in the samples since at this pressure the sample has not
137 undergone a complete phase transition to the DR phase [24,28]. In the second
138 experiment, we increased pressure up to 30.8 GPa in order to induce a total cation-
139 vacancy disorder, transforming our sample to the opaque DR structure, as shown in
140 previous high-pressure XRD and RS measurements in DC-HgGa₂Se₄ [24,28]. In both
141 experiments, pressure was slowly decreased to 1.0 GPa after the first upstroke to study
142 the reversibility of the bandgap energy and of the defects created during the first
143 upstroke. In summary, the main difference between both experiments is the maximum
144 pressure reached (15.4 and 30.8 GPa) which influences the completion of the phase
145 transition to the opaque DR phase observed in previous experiments above 17-22 GPa
146 depending on the technique used and the hydrostatic conditions of the experiment
147 [24,28]. We will show that the study of the optical absorption of the recovered samples
148 from both experiments show important differences in order to understand pressure-
149 induced order-disorder processes in OVCs.

150

151 **3. Results and discussion**

152 Our aim is to show that high-pressure optical absorption measurements on DC-
153 HgGa₂Se₄ evidence changes in the optical properties that correlate with changes in the
154 structural and vibrational properties already seen in previous high-pressure XRD and
155 RS experiments carried out under similar conditions [24,25,28]. Therefore, hereafter we
156 will explain the results of our high-pressure optical absorption experiments by
157 correlating them with the different phases of HgGa₂Se₄ discussed in previous works
158 (DC, DS, DR, and DZ).

159 **Figure 1** shows a selection of the optical absorption spectra in DC-HgGa₂Se₄
160 during the first upstroke up to 15.4 GPa. As it can be observed, there is a blue shift of
161 the fundamental absorption edge with increasing pressure up to 11.2 GPa and a red shift
162 between this pressure and 15.4 GPa. At pressures higher than 14.8 GPa, the presence of
163 a great number of dark linear defects in the sample results in an almost complete
164 darkening of the samples and a very large low-energy tail in the absorption spectra due
165 to light absorption by defects. Therefore, the estimation of the direct bandgap energy
166 has not been possible above 14.8 GPa.

167 As commented in a previous work, a low-energy tail begins to appear in the
168 optical absorption spectrum of DC-HgGa₂Se₄ around 11.8 GPa [21]. The appearance of

169 a low-energy tail in the optical absorption spectrum of a direct bandgap semiconductor
170 could be attributed to: i) the observation of an indirect bandgap below the direct
171 bandgap due to a direct-to-indirect bandgap crossover [43, 44, 47] or ii) optical
172 absorption by defects which are precursors of a phase transition [44, 48, 49]. In this
173 respect, *ab initio* calculations for DC-HgGa₂Se₄ reported in **Ref. 21** concluded that the
174 bandgap is of direct type and that a direct-to-indirect bandgap crossover would only
175 occur at pressures higher than 16 GPa; i.e., at pressures at which the bandgap cannot be
176 estimated experimentally because of the light absorption by defects. Therefore, the
177 appearance of the low-energy tail observed between 12 and 16 GPa in HgGa₂Se₄ cannot
178 be attributed to the indirect bandgap. This situation is similar to that of DC-CdGa₂Se₄
179 above 6-8 GPa [23].

180 **Figure 2** shows images taken during the second experiment up to 30.8 GPa. It
181 can be observed that the original DC-HgGa₂Se₄ sample presents a reddish color at 0.6
182 GPa and that on increasing pressure to 11.8 GPa the sample becomes more transparent.
183 Above this pressure, dark linear defects, which are precursors of a phase transition,
184 appear together with the appearance of the low-energy tail. At 30.8 GPa the sample
185 appears black in color because of the completion of the phase transition to the opaque
186 DR phase.

187 **Figure 3** shows the pressure dependence of the direct bandgap energy (circles)
188 in DC-HgGa₂Se₄ during the first upstroke which is estimated by extrapolating the linear
189 fit of the high-energy part of the $(\alpha \cdot hv)^2$ vs. hv plot to zero absorption. Inset of **Fig. 1**
190 shows a plot of $(\alpha \cdot hv)^2$ vs. hv where the tangent method is applied to estimate the direct
191 bandgap energy of DC-HgGa₂Se₄ from the absorption coefficient at 0.6 GPa in the first
192 upstroke. Error bars for the bandgap energies have been estimated by taking into
193 account the different ranges of absorption coefficient values for which the relationship
194 $(\alpha \cdot hv)^2$ vs. hv is linear at each different pressure. These different ranges of the
195 absorption coefficient values give different values of the bandgap energy depending on
196 the slope of the straight line obtained from the linear fit. Note that the error bar for the
197 bandgap energy increases at pressures above 11.8 GPa due to the presence of the low-
198 energy tail. In **Fig. 3** can be observed that the direct bandgap energy of DC-HgGa₂Se₄
199 exhibits a strong non-linear pressure dependence up to 8 GPa. This behavior was
200 already observed in DC-HgGa₂Se₄ and also in DC-CdGa₂Se₄ and explained on the basis
201 of theoretical *ab initio* calculations which demonstrated that this non-linear behavior is

202 a general feature common to all OVCs [21]. In particular, it was proposed that this
203 behavior was due to a conduction band anticrossing at the Γ point of the Brillouin zone
204 caused by two factors: i) the presence of ordered vacancies in adamantine OVCs and ii)
205 the doubling of the unit cell along the c axis with respect to the zincblende structure.

206 It can be observed that the direct bandgap energy in DC-HgGa₂Se₄ increases at
207 low pressures with a pressure coefficient of 31 ± 4 meV/GPa estimated from a linear fit
208 in the range 0.6-2.9 GPa (see blue line in **Fig. 3**), while at pressures above 11.8 GPa the
209 bandgap energy decreases with a pressure coefficient of -20 ± 3 meV/GPa estimated
210 from a linear fit in the range 11.8-14.8 GPa (see pink line in **Fig. 3**). We note that a
211 rough estimate of the pressure coefficient of the direct bandgap can also be obtained by
212 measuring the shift of the optical absorption edge at a constant high absorption
213 coefficient. Following this procedure, the pressure coefficients obtained for the direct
214 bandgap energy of DC-HgGa₂Se₄ at low pressure in the range 0.6-2.9 GPa and at high
215 pressure in the range 11.8-14.8 GPa are 31 ± 1 and -20 ± 6 meV/GPa, respectively; which
216 agree with those previously obtained from the linear extrapolation method. A similar
217 behavior was observed in DC-CdGa₂Se₄ [21,23], and the gradual decrease of its direct
218 bandgap above 6-8 GPa was interpreted as a signature of the onset of the cation disorder
219 process that gradually transforms the DC phase to a structure with a partial disorder
220 which was tentatively attributed to a DS structure [23].

221 We must note that a change in the sign of the pressure coefficient of the direct
222 bandgap above certain pressure was already noted in some chalcopyrites, like CuAlSe₂
223 [50], and in defect zincblende compounds, like Ga₂Se₃ [51]. In these works, the change
224 of sign of the pressure coefficient was attributed either to a direct-pseudodirect bandgap
225 crossover [50] or to a direct-indirect bandgap crossover [51]. In this respect, we have
226 discarded these two interpretations, as has been previously commented, because we
227 have performed band structure calculations in DC-HgGa₂Se₄ (see Ref. 21) and our
228 calculations do not support the direct-indirect bandgap crossover as the origin of the
229 decrease of the bandgap above 11.2 GPa in DC-HgGa₂Se₄. Moreover, we must note that
230 in DC-HgGa₂Se₄ the appearance of a low-energy tail in the optical absorption spectrum
231 begins around 12 GPa which is coincident with the onset of a stronger decrease of the
232 bandgap energy as in DC-CdGa₂Se₄ [23]. Therefore, we may attribute both the abrupt
233 decrease of the bandgap energy in DC-HgGa₂Se₄ and the appearance of the low-energy
234 tail around 12 GPa to the onset of the cation-cation or cation-vacancy disorder

235 processes. This process gradually transforms the initial DC phase of HgGa_2Se_4 first to a
236 structure with partial cation disorder, tentatively attributed to a DS phase [28], and then
237 at higher pressures to a structure with full cation-vacancy disorder and considered to be
238 the DR phase [24,28].

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

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

280 As regards the nature of the sample recovered from 15.4 GPa, it is known that
281 ZnGa_2Se_4 samples with partial cation or cation-vacancy disorder, like those crystallizing
282 in the DS structure, show a slightly smaller bandgap energy than ordered samples of the
283 DC structure [30]. Therefore, the smaller decrease of the direct bandgap in the sample
284 recovered from 15.4 GPa than that recovered from 30.8 GPa, prompts to attribute it to a
285 structure with an intermediate degree of disorder between that of DC and DZ structures.
286 In this respect, different intermediate structures between these two structures have been
287 recently discussed [53]. In particular, a phase with a possible DS structure (likely model
288 7 of Ref. 53 where cations and vacancies become partially mixed) was found in RS
289 measurements of DC- HgGa_2Se_4 above 19 GPa [28]. This DS phase shows more Raman
290 peaks than the DC phase because of the partial occupation of the vacancy position [28].
291 However, the disappearance of the A_2 Raman mode (characteristic of the DC structure)
292 observed above 14.5 GPa in HgGa_2Se_4 [28] suggests that a DS phase is already formed
293 at this pressure which is different from the previous DS phase since no new Raman
294 modes are present [28]. The DS phase of HgGa_2Se_4 above 14.5 GPa is likely to be
295 similar to that already observed in CdGa_2Se_4 (model 2 or 6 of Ref. 53 where cations and
296 vacancies are not mixed) [23]. Since the onset of structural disorder in HgGa_2Se_4 is
297 observed above 12 GPa, we consider that pressures above 12-13 GPa are high enough to
298 observe the irreversibility of the pressure-induced disorder process in DC- HgGa_2Se_4 .
299 Consequently, hereafter we will consider that the sample obtained after pressurization of
300 DC- HgGa_2Se_4 to 15.4 GPa is a partially-disordered DS structure likely corresponding to
301 model 2 or 6 of Ref. 53.

302 **Figure 4** shows selected optical absorption spectra of the two samples with DS
303 and DZ structures recovered from 15.4 GPa and from 30.8 GPa, respectively. These
304 measurements were obtained during a second upstroke after recovering the samples to
305 pressures near 1 GPa. In both recovered samples the optical absorption edge exhibits a
306 blue shift with increasing pressure more pronounced for the case of the DS phase. DS
307 and DZ samples exhibit a progressive darkening above 6-8 GPa that prevents a good
308 measurement of the optical absorption spectrum at higher pressures. In fact, a complete
309 darkening of the DS and DZ samples was observed around 14 GPa. This last pressure is
310 in agreement with the pressure (16 GPa) at which RS measurements, performed during
311 a second upstroke in a DZ-HgGa₂Se₄ sample recovered from the DR phase, showed no
312 Raman activity as expected after the transition to the DR phase [28]. Therefore, on the
313 basis of these results we tentatively attribute the high-pressure structure of the DS and
314 DZ phases, found at pressures above those in which we observe the complete darkening
315 of the samples, to the same octahedrally-coordinated DR structure previously observed
316 upon compression of the DC phase during the first upstroke [24,28]. It must be stressed
317 that the smaller pressure for the DS→DR and DZ→DR phase transitions than for the
318 DC→DR phase transition is in good agreement with the order-disorder mechanism of
319 the transitions from the DC, DS and DZ phases to the completely disordered DR phase;
320 i.e., the larger the disorder in the initial sample the smaller the phase transition pressure
321 to the fully disordered high-pressure structure.

322 From the optical absorption measurements performed in the two recovered
323 samples at different pressures we have estimated the direct bandgap energy of the
324 samples with DS and DZ structures as a function of pressure by extrapolating the linear
325 fit of the high-energy part of the $(\alpha \cdot hv)^2$ vs. hv plot to zero absorption. Inset of **Fig. 4**
326 shows a plot of $(\alpha \cdot hv)^2$ vs. hv where the tangent method is applied to estimate the direct
327 bandgap energy of DS-HgGa₂Se₄ from the absorption coefficient at 0.9 GPa in the
328 second upstroke. The results for the direct bandgap energy of the DS and DZ phases up
329 to 6-8 GPa are shown in **Fig. 3** with squares and triangles, respectively. Note that
330 theoretical calculations support the existence of a direct bandgap at smaller energy than
331 the indirect bandgap in all OVCs (including those with DS and pseudocubic structures)
332 at ambient pressure [21] and the same feature is expected for the DZ phase, as it occurs
333 in most binary zincblende-type compounds [54]. The experimental pressure coefficient
334 of the direct bandgap energy of DZ-HgGa₂Se₄ at low pressure has been estimated from

335 a linear fit in the range 1.0-3.8 GPa to be around 7 ± 3 meV/GPa while the pressure
336 coefficient at low pressure of the direct bandgap energy of the DS sample recovered
337 from 15.4 GPa has been estimated from a linear fit in the range 0.9-3.9 GPa to be
338 around 24 ± 6 meV/GPa. As it has been previously commented, we have also obtained
339 the pressure coefficient of the direct bandgap energy by measuring the shift of the
340 optical absorption edge at a constant high absorption coefficient. Following this
341 procedure, the pressure coefficients obtained for the direct bandgap energy of the DZ
342 and DS phases of HgGa_2Se_4 at low pressure in the ranges 1.0-3.8 GPa and 0.9-3.9 GPa
343 are 6 ± 3 and 22 ± 2 meV/GPa, respectively; which are in good agreement with those
344 obtained with the linear extrapolation method. Both pressure coefficients for the
345 recovered phases are smaller than that of the DC phase at low pressure (31 ± 4
346 meV/GPa), and much smaller than the pressure coefficients at low pressure of binary
347 zincblende-type compounds, in particular ZnSe (70 meV/GPa [55,56]) and HgSe (43
348 meV/GPa [56,57]). Therefore, our results show that there is a clear decrease of the
349 direct bandgap energy and its pressure coefficient with increasing disorder in OVCs. In
350 the following we will try to explain the reason for these two features of disordered
351 phases in OVCs.

352 In order to address the explanation of the above mentioned features, we have to
353 consider the parallelism between the properties of ternary ABX_2 chalcopyrites and
354 AB_2X_4 OVCs since both families of tetragonal compounds derive from the cubic
355 zincblende structure. In these two tetragonal families, the different values of the
356 bandgap energy of compounds with the same composition but different structures could
357 be determined by three main factors: i) tetragonal distortion of the crystal lattice, as
358 described by the deviation of the axial c/a ratio from 2 (external distortion); ii)
359 displacement of anions from the ideal position in the zincblende structure (internal
360 distortion); and iii) cation-cation disorder (in chalcopyrites) and cation-cation or cation-
361 vacancy disorder (in OVCs) [2]. It is well known that increasing disorder in
362 chalcopyrites leads to the DZ structure with a smaller bandgap energy than that of the
363 chalcopyrite structure [50,52,58]. On the other hand, it has been commented that
364 increasing disorder in OVCs leads to a negligible increase of the unit cell volume
365 through a decrease of the tetragonal distortion (external distortion) and the tendency of
366 anions on average towards the ideal position (internal distortion) in the zincblende
367 structure [59]. Therefore, the decrease in the bandgap energy of chalcopyrites with
368 increasing disorder cannot be ascribed to either the internal or external distortion and

369 must be mainly ascribed to cation-cation disorder. This argument can be also
370 extrapolated to ternary AB_2X_4 OVCs since the theoretical direct bandgap energy in these
371 OVCs is only slightly changed by the modified structural parameters on going from the
372 DC structure towards the DZ structure [4]. In fact, the decrease of the bandgap in the
373 disordered phases of OVCs is observed irrespective of the volume of the DZ and DC
374 phases as measured from XRD measurements. Note that DZ-CdGa₂Se₄ has a larger
375 volume than DC-CdGa₂Se₄ [10] while DZ-HgGa₂Se₄ has a smaller volume than DC-
376 HgGa₂Se₄ [24] but both compounds show a smaller bandgap in the DZ phase than in the
377 DC phase. Therefore, we should ascribe the change in the direct bandgap energy of
378 different structures in ternary AB_2X_4 OVCs mainly to the effect of cation or cation-
379 vacancy disorder in complete parallelism with chalcopyrite compounds.

380 On the basis of the previous considerations, we have come to the conclusion that
381 the decrease of the bandgap energy with increasing disorder in ternary AB_2X_4 OVCs,
382 like CdGa₂Se₄ and HgGa₂Se₄ can be explained in the same way as it was previously
383 explained in chalcopyrites [59]; i.e. by the level repulsion effect responsible for bandgap
384 bowing in alloys [60,61] and by the formation of donor and acceptor pairs which lead to
385 donor-like and acceptor-like bands inside the parent bandgap of the ordered compound
386 [59]. On one hand, a small disorder in OVCs, like that occurring when going from DC
387 to DS phases, leads to a small decrease of the bandgap energy because of the small
388 repulsion effect between levels and the presence of relatively shallow donor-like and
389 acceptor-like levels inside the bandgap of the parent DC phase. On the other hand, a
390 larger disorder in OVCs, like that occurring in the DZ phase with a total cation-vacancy
391 disorder in cation sites of the zincblende phase, leads to a larger decrease of the bandgap
392 energy because of the larger repulsion effect between levels and the presence of deep
393 donor-like and acceptor-like levels inside the bandgap of the parent DC phase.

394 We will discuss now the values of the pressure coefficients of the direct bandgap
395 in the DS and DZ phases. In order to explain the pressure coefficient of the direct
396 bandgap energy in DS-HgGa₂Se₄, which is intermediate between those of the DC and
397 DZ phases, we want to stress that the DS phase is a tetragonal OVC and has two
398 lowermost conduction bands, like the DC phase [21]. The smaller pressure coefficient
399 of the direct bandgap energy in the DS phase with respect to the DC phase can be
400 explained by considering that the bandgap energy of the DS phase is determined by the
401 bands formed by shallow donors and acceptors, which arise during the transition from
402 the DC to the DS phase. These donor-like and acceptor-like bands should have similar

403 pressure coefficients than the lowermost conduction and topmost valence band,
404 respectively. Finally, one has to take into account that the lowermost conduction band in
405 the DS phase is expected to have a larger proportion of Ga cations located at $2a$ sites
406 than in the DC phase, which mainly contribute to the second conduction band of the DC
407 phase [21]. Since the second conduction band of the DC phase has a smaller pressure
408 coefficient than the first conduction band [21], the disorder of Hg cations at $2d$ sites and
409 Ga cations at $2a$ sites, as it would occur in model 2 of the DS phase in Ref. 53, would
410 result in a larger contribution of Ga($2a$) atoms to the lowermost conduction band than in
411 the DC phase and consequently this would yield a smaller pressure coefficient of the
412 direct bandgap energy in the DS phase than in the DC phase. In this sense, it must be
413 stressed that model 6 of DS phase (in which Hg at $2d$ sites and Ga at $2c$ sites; i.e.,
414 located at the same cation plane perpendicular to the c axis, get mixed) is expected to
415 have roughly the same pressure coefficient than the DC phase since both Hg($2d$) and
416 Ga($2c$) atoms mainly contribute to the lowermost conduction band [21]. Therefore, our
417 optical absorption measurements lead us to consider that the DS phase recovered in
418 HgGa₂Se₄ from 15.4 GPa likely corresponds to model 2 of Ref. 53 where some Hg($2d$)
419 atoms occupy Ga($2a$) positions at the same plane as vacancies (located at $2b$ Wyckoff
420 sites).

421 Finally, the much smaller pressure coefficient of the bandgap energy in the DZ
422 phase compared to the parent DC phase can be explained by the presence of deep
423 acceptors and donors in the DZ phase. It is known that deep levels inside the bandgap
424 (either with donor or acceptor character) have very small pressure coefficient, owing to
425 the nature of the localized close-range potential binding electrons, that is more
426 determined by atomic electronegativity differences than by the crystal band structure
427 [62, 63]. Therefore, the formation of deep donor-like and acceptor-like bands in the DZ
428 phase reduce considerably both the bandgap energy and its pressure coefficient.

429 The above conclusion is supported by our theoretical calculations of the direct
430 bandgap energy on CdGa₂Se₄ and HgGa₂Se₄ both in the DC (I-4) phase and in the ideal
431 zincblende phase without disorder as performed in Ref. [4] (see Ref. 21 for theoretical
432 details of our *ab initio* calculations). Note that the ideal zincblende phase was simulated
433 for different volumes taking as basis a I-4 unit cell where the c parameter was fixed to
434 $c=2a$ and where the anion, located at the $8g$ Wyckoff position, was fixed at
435 $(1/4,1/4,1/8)$. In general, our calculations have confirmed the results of Ref. [4] and
436 have shown that the pressure coefficient of the direct bandgap energy in the ideal

437 zincblende phase without disorder, for both compounds, is twice the pressure coefficient
438 in the DC phase. This result is in complete contradiction to our experimental results
439 which show a considerable decrease of the pressure coefficient of the direct bandgap
440 energy in the DZ phase with respect to the DC phase; therefore, we can conclude that
441 the decrease of the pressure coefficient of the direct bandgap energy observed in the DZ
442 phase must be mainly ascribed to the effect of disorder.

443 We want to clarify that the explanation we have provided in this work for the
444 decrease of the direct bandgap energy and its pressure coefficient in the DZ phase of
445 ternary AB_2X_4 OVCs is in contrast to that provided in a previous work related to DC-
446 $CdGa_2Se_4$ [23]. In that work it was considered that the smaller bandgap of the
447 disordered DZ phase was mainly due to the larger unit cell volume of the DZ phase with
448 respect to the DC phase and that the decrease of the pressure coefficient of the direct
449 bandgap was due to the uneven mixture of the two lowermost conduction bands of the
450 DC phase which contribute to the lowermost conduction band in the DZ phase. In this
451 respect, we have to note that we have modified our view in this work on the light of the
452 literature existing for ABX_2 compounds and the results which point to a negligible
453 volume change with increasing disorder in ternary AB_2X_4 OVCs. In summary, we
454 conclude that both the smaller direct bandgap energy and its smaller pressure coefficient
455 in the DZ phase than in the DC phase can be explained by taking into account the deep
456 acceptor-like and donor-like bands formed due to cation and cation-vacancy disorder
457 present in the DZ phase of OVCs.

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461 **4. Conclusions**

462 We have performed optical absorption measurements in tetragonal defect
463 chalcopyrite (DC) $HgGa_2Se_4$ (S.G. $I-4$) under high pressure. Two types of experiments
464 performed in this ordered-vacancy compound below and above 20 GPa have shown the
465 importance of the maximum pressure applied to a defect chalcopyrite sample in order to
466 understand the effects of pressure-induced order-disorder processes on recovered
467 samples. If applying pressure leads to a total cation-vacancy disorder, as in the cubic
468 disordered rocksalt (DR) phase (S.G. $Fm-3m$), the sample usually returns on
469 decompression to a cubic disordered zincblende (DZ) structure (S.G. $F-43m$), also with

470 total cation-vacancy disorder, showing the smallest direct bandgap and pressure
471 coefficient. However, if pressure is not high enough to complete the phase transition to
472 the DR phase the sample undergoes a partial cation-cation or cation-vacancy disorder
473 and on decreasing slowly pressure the sample returns to a structure with a bandgap
474 energy and pressure coefficient intermediate between those of the DC and DZ phases
475 which we have attributed to a tetragonal disordered stannite (DS) (S.G. *I-42m*) phase
476 (model 2 of **Ref. 53**) in HgGa_2Se_4 . The reason why the direct bandgap energy and its
477 pressure coefficient for the disordered phases (DS and DZ) of OVCs are smaller than
478 those inherent to the parent ordered DC phase has been explained by the level repulsion
479 effect responsible for bandgap bowing in alloys and by the formation of donor and
480 acceptor pairs in the DS and DZ phases which lead to donor-like and acceptor-like
481 bands inside the parent bandgap of the ordered compound.

482

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608 the direct bandgap in zincblende-type HgSe. The value given in the text is a theoretical
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610 agreement with experimental results (**see table V in Ref. 56**).
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618 **Figure captions**

619 **Figure 1.** Optical absorption edge of DC-HgGa₂Se₄ on increasing pressure up to 10.4
620 GPa (a) and from 10.4 up to 15.4 GPa (b). Inset shows a plot of $(\alpha \cdot hv)^2$ vs. hv where the
621 tangent method is applied to estimate the direct bandgap energy of DC-HgGa₂Se₄ from
622 the absorption coefficient at 0.6 GPa in the first upstroke.

623 **Figure 2.** (Color online) Sequence of photographs of the HgGa₂Se₄ crystal taken during
624 the first upstroke of the second experiment at 0.6, 11.8, and 30.8 GPa. The last
625 photograph was taken at 2.9 GPa during the second upstroke of the second experiment.

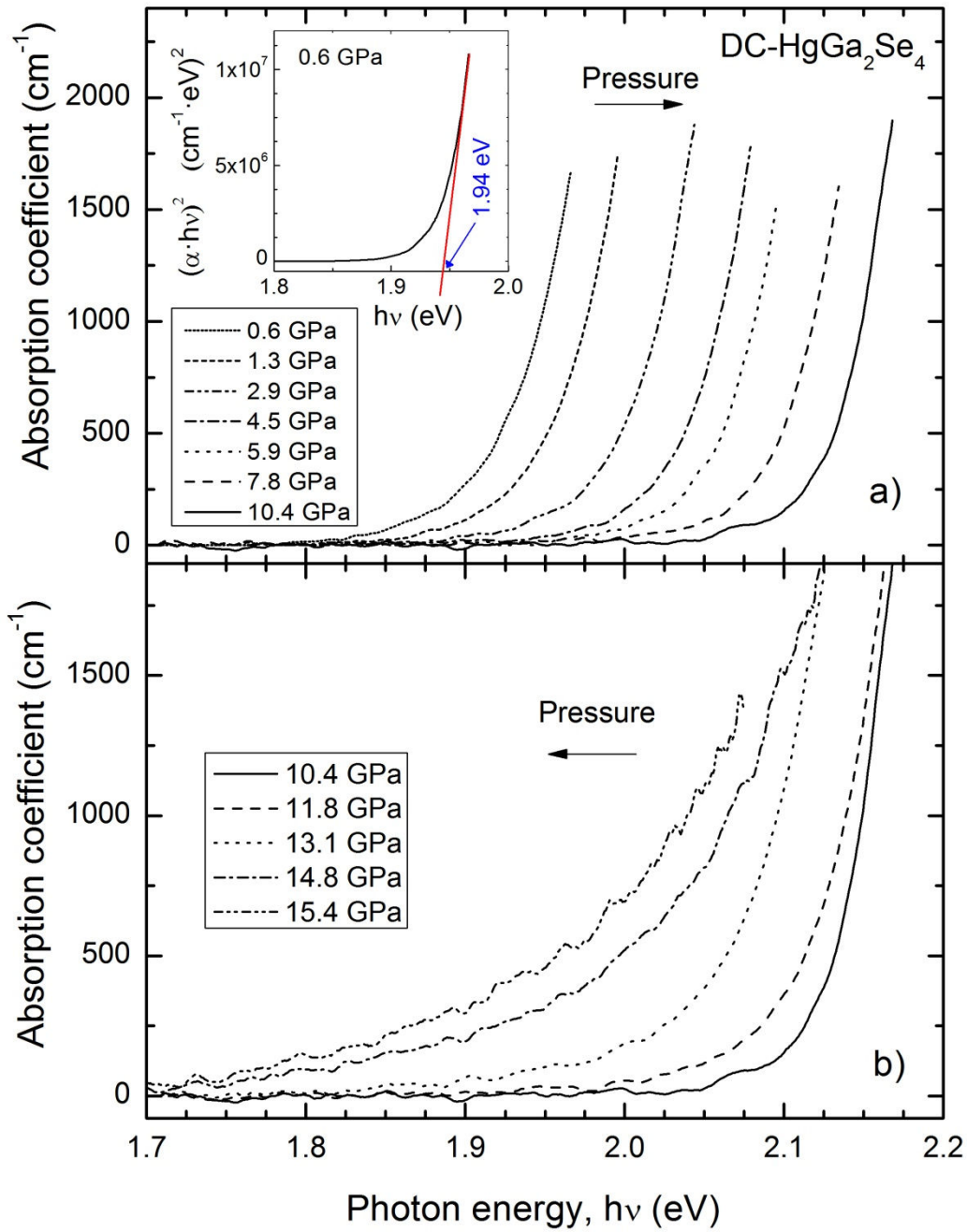
626 **Figure 3.** (Color online) Pressure dependence of the bandgap energy in the different
627 phases of HgGa₂Se₄. Circles with error bars are obtained during a first upstroke.
628 Triangles with error bars, and squares with error bars are obtained during a second
629 upstroke in recovered DZ and DS samples after increasing pressure during a first
630 upstroke up to 30.8 and 15.4 GPa, respectively. Experimental values of pressure
631 coefficients of the direct bandgaps at low pressure (in the DC, DS and DZ phases) and
632 at high pressure (in the DC phase) are also shown. Coloured solid lines are just guides
633 to the eye for establishing the slopes of the bandgaps in the different structures of
634 HgGa₂Se₄ and are not related to any kind of phase transition in this compound.

635 **Figure 4.** Pressure dependence of the optical absorption edge of the recovered samples
636 of HgGa₂Se₄ measured during a second upstroke in the first (a) and second (b)
637 experiment; i.e., after having increased pressure in the first upstroke up to 15.4 GPa and
638 up to 30.8 GPa, respectively. Inset shows a plot of $(\alpha \cdot hv)^2$ vs. hv where the tangent
639 method is applied to estimate the direct bandgap energy of DS-HgGa₂Se₄ from the
640 absorption coefficient at 0.9 GPa in the second upstroke.

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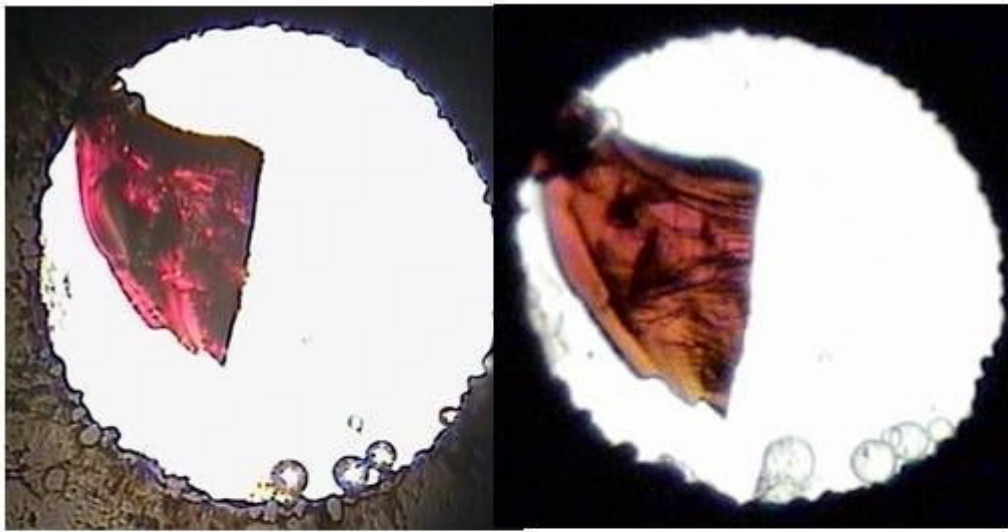
642 **Figure 1**

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646 **Figure 2**



0.6 GPa

11.8 GPa



30.8 GPa

2.9 GPa

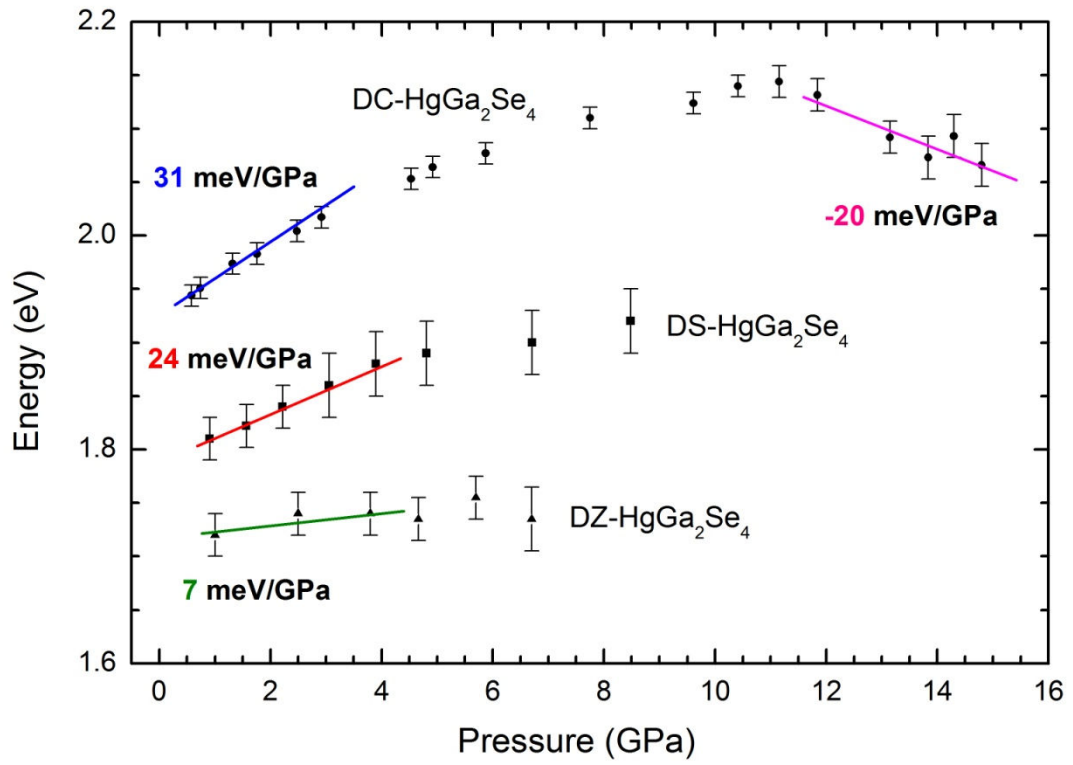
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651 **Figure 3**



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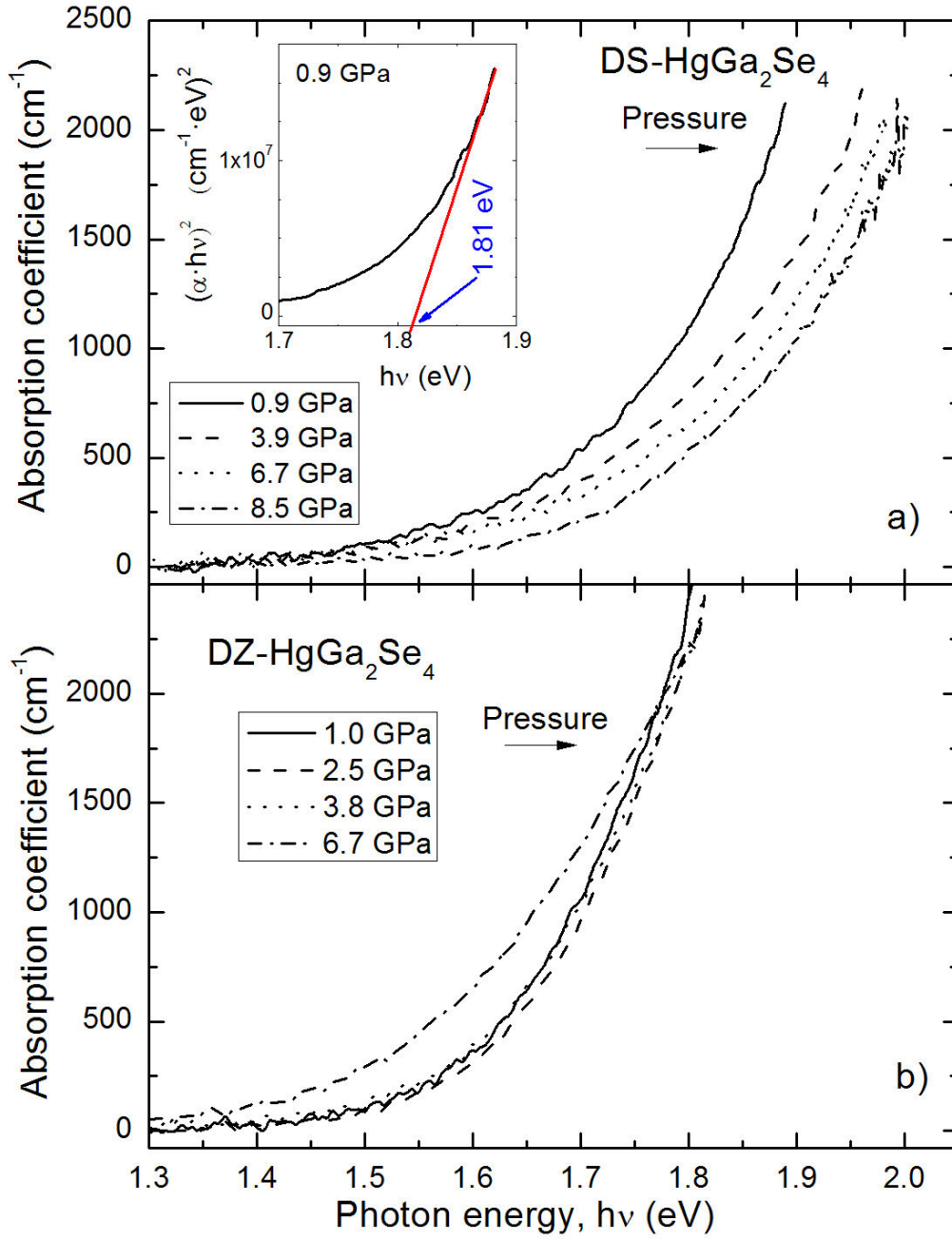
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