



# Pressure-induced band anticrossing in two adamantine ordered-vacancy compounds: CdGa<sub>2</sub>S<sub>4</sub> and HgGa<sub>2</sub>S<sub>4</sub>



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## ABSTRACT

This paper reports a joint experimental and theoretical study of the electronic band structure of two ordered-vacancy compounds with defect-chalcopyrite structure: CdGa<sub>2</sub>S<sub>4</sub> and HgGa<sub>2</sub>S<sub>4</sub>. High-pressure optical-absorption experiments (up to around 17 GPa) combined with first-principles electronic band-structure calculations provide compelling evidence of strong nonlinear pressure dependence of the bandgap in both compounds. The nonlinear pressure dependence is well accounted for by the band anticrossing model that was previously established mostly for selenides with defect chalcopyrite structure. Therefore, our results on two sulfides with defect chalcopyrite structure under compression provide definitive evidence that the nonlinear pressure dependence of the direct bandgap is a common feature of adamantine ordered-vacancy compounds and does not depend on the type of anion.

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## 1. Introduction

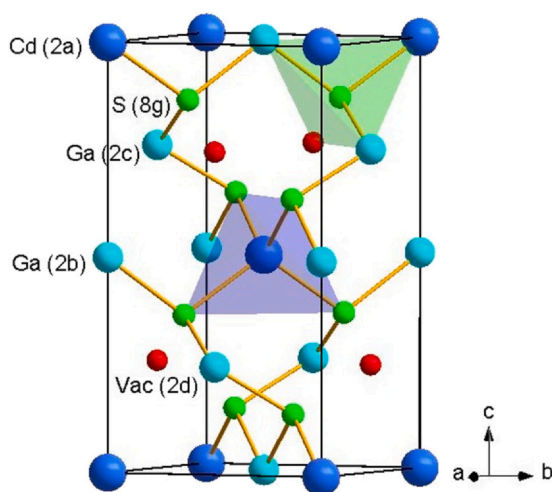
CdGa<sub>2</sub>S<sub>4</sub> and HgGa<sub>2</sub>S<sub>4</sub> belong to the well-known family of ordered vacancy compounds (OVCs) and have the chemical formula A<sup>II</sup>B<sub>2</sub><sup>III</sup>X<sub>4</sub><sup>VI</sup>. These compounds are analogous to ternary adamantine semiconductors A<sub>n</sub>B<sub>4-n</sub>X<sub>4</sub> formed either in pseudo-cubic structure (PC, *P4̄2m*, including layered CuAu I-like and Cu<sub>3</sub>Au-like structure), famatinitite structure (*I4̄2m*) or chalcopyrite structure (*I4̄*) according to the composition ratios of the factor “n” and stack sequence of the ternary zinc-blende compounds AX and BX in A<sub>n</sub>B<sub>4-n</sub>X<sub>4</sub> compounds [1,2]. The crystal structure of OVCs with A<sup>II</sup>B<sub>2</sub><sup>III</sup>X<sub>4</sub><sup>VI</sup> stoichiometry is formed by removing some of the A-type cations in ternary adamantine A<sub>n</sub>B<sub>4-n</sub>X<sub>4</sub> compounds in order to balance the charge. For instance, by removing alternately one base-centered and four corner A cations of the famatinitite structure of A<sub>2</sub>B<sub>2</sub>X<sub>4</sub> compounds one can form defect-famatinitite (DF) or defect stannite (DS) structure of OVCs. On the other hand, the defect chalcopyrite (DC) structure of

OVCs can be derived by removing the same site in the chalcopyrite structure of A<sub>2</sub>B<sub>2</sub>X<sub>4</sub> compounds [2]. In this context, OVCs play an important role in fundamental research on how physical and chemical properties of solid-state materials can be affected by vacancies and their different orderings.

Thanks to the existence of an ordered array of vacancies in OVCs, they exhibit wide bandgap, high photosensitivity, bright photoluminescence and long-term stability of many parameters. Therefore, OVCs exhibit a strong potential application on solar cells [3], optoelectronic devices, temperature sensors and nonlinear optics [2,4–10]. In particular, CdGa<sub>2</sub>S<sub>4</sub> and HgGa<sub>2</sub>S<sub>4</sub> are transparent in a wide wavelength range (around 0.5–13 μm) and show a high figure of merit [11]. The second harmonic coefficient d<sub>36</sub> of HgGa<sub>2</sub>S<sub>4</sub> has been determined to be 5 times larger than the d<sub>31</sub> value in LiNbO<sub>3</sub> and show an unusual large birefringence [12]. Besides, HgGa<sub>2</sub>S<sub>4</sub> is also suitable for frequency conversion of visible, near, and mid-IR lasers [13]. Furthermore, except for the ordered-vacancy, the transition metal sulfide also play an important role in the application of those two compounds, which have been wildly investigated due to the promising catalytic activity [14–17].

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**Fig. 1.** Crystal structure of defect chalcopyrite  $\text{CdGa}_2\text{S}_4$ . The red ball represents the position of vacancy ("Vac" in figure). A replacement of Cd in the (2c) position by Hg results in the defect chalcopyrite  $\text{HgGa}_2\text{S}_4$ .

At ambient pressure,  $\text{CdGa}_2\text{S}_4$  was reported in the DC structure as shown in Fig. 1 with lattice parameters:  $a = 5.553(1)$  Å and  $c = 10.272$  Å [18]. At normal conditions, its bandgap was reported to be 3.44 eV [19] and subsequent calculations showed that the nature of bandgap is direct at the  $\Gamma$  point of first Brillouin zone [4,20]. High-pressure x-ray diffraction (HP-XRD) measurements were reported to investigate the high-pressure structural behavior of  $\text{CdGa}_2\text{S}_4$  [21]. The tetragonal DC structure was shown to be stable up to 17 GPa and an irreversible phase transition occurred beyond this pressure. The high-pressure phase was proposed to be a defect-cubic NaCl-type (disordered rock-salt, DR) structure ( $\text{Fm}\bar{3}\text{m}$ ). In other words,  $\text{CdGa}_2\text{S}_4$  undergoes a DC-to-DR phase transition. The experimental bulk modulus reported for  $\text{CdGa}_2\text{S}_4$  was 64 (2) GPa [21] while the theoretical ones are 40.8 GPa [22] and 46 GPa [23]. High-pressure Raman scattering (HP-RS) measurements were also reported by Ursaki et al. in 1999 [24], Mitani et al. in 2001 [25], and Gallego-Parra et al. in 2019 [22], respectively. Both Ursaki's and Mitani's works reported two order-disorder stages leading from the DC structure to a Raman-inactive phase. In both works, the pressure of the first and second order-disorder stages occurred at 8 and 10 GPa, respectively. The DC to Raman-inactive phase transition can be considered to be related to the DC-to-DR phase transition found in HP-XRD experiments since the DR phase is Raman inactive. However, the DC-to-DR phase transition is irreversible in Ursaki's work and reversible in Mitani's work, despite in both works the phase transition is between 14 and 15 GPa. In the paper reported by Gallego-Parra et al., authors found an irreversible DC-to-DR phase transition, whose onset is around 15 GPa, and interpreted that there was only a single pressure-induced order-disorder stage above 9 GPa that was attributed to the phase transition from the DC phase to an intermediate defect-stannite (DS) phase prior to the DR phase. Therefore, this result contrasted with the two previous HP-RS works. A complete detail of order-disorder stages expected in OVCs; in particular those leading from the DC phase to the DR phase, was already reported [26].

$\text{HgGa}_2\text{S}_4$  also crystallizes at normal conditions in the DC structure (Fig. 1) with lattice parameters  $a = 5.5106(1)$  Å and  $c = 10.2392(2)$  Å [27]. The direct bandgap of DC- $\text{HgGa}_2\text{S}_4$  reported at ambient pressure is around 2.84 eV [28,29]. HP-RS measurements on DC- $\text{HgGa}_2\text{S}_4$  [30] found the evidence of the pressure-induced phase transition from the completely ordered DC structure to a partially disordered DS structure above 18 GPa, and then followed by an irreversible transition to the completely disordered DR phase above 23 GPa. HP-XRD measurements conducted in DC- $\text{HgGa}_2\text{S}_4$  up to 15.1 GPa [31], estimated the bulk modulus to be 48.4(3) GPa by using

a third-order Birch-Murnaghan equation of state [32] to fit volume-pressure data up to 10 GPa. No phase transition was found in the whole experimental range, despite theoretical calculations predicted that the DC phase of  $\text{HgGa}_2\text{S}_4$  becomes mechanically unstable above 13.8 GPa.

To complete the above studies, we report in this work an experimental and theoretical study of the electronic band structure of two sulfur-based OVCs with DC structure ( $\text{CdGa}_2\text{S}_4$  and  $\text{HgGa}_2\text{S}_4$ ) under compression up to around 17 GPa by means of HP optical absorption measurements combined with first-principle electronic band structure calculations. We will show that the bandgap of both compounds exhibits a strong nonlinear behavior as a function of pressure, supporting the common feature of adamantite OVCs provided by previous HP studies of the electronic band structure on  $\text{CdGa}_2\text{Se}_4$  and  $\text{HgGa}_2\text{Se}_4$  [33],  $\text{Ga}_2\text{Se}_3$  [34], and  $\text{Ga}_2\text{S}_3$  [35]. The theoretical calculated electronic band structure and related HP crystal structure behavior were used to reveal the reason for the strong nonlinear behavior of the bandgap under pressure in comparison with the previously reported HP band gap energy behavior of several OVCs.

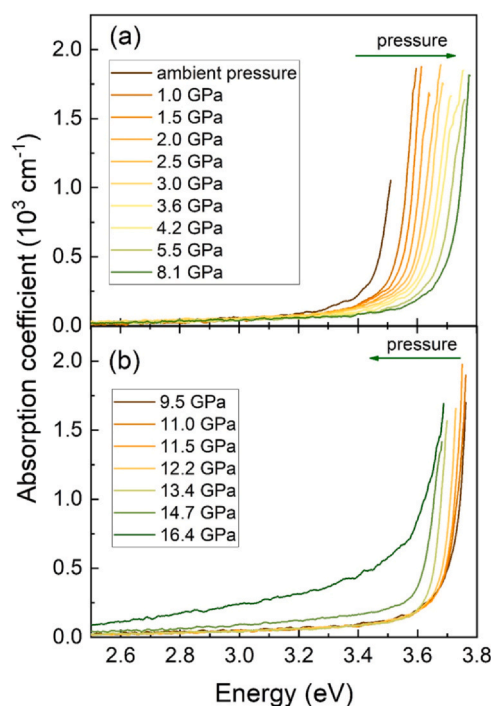
## 2. Methods

### 2.1. Experimental details

Single crystals of  $\text{CdGa}_2\text{S}_4$  and  $\text{HgGa}_2\text{S}_4$  grown from its constituents CdS (HgS) and  $\text{Ga}_2\text{S}_3$  by the chemical vapor transport method using iodine as transport agent [24,29], were used in the high-pressure optical-absorption experiments. A 4:1 methanol-ethanol mixture, acting as a pressure-transmitting medium (PTM), and a single crystal sample with a thickness around 20  $\mu\text{m}$  were loaded together in a 250  $\mu\text{m}$  hole performed in a stainless-steel gasket pre-indented to a thickness of 50  $\mu\text{m}$  inside a membrane-driven diamond-anvil cell (DAC) with diamond culets of 500  $\mu\text{m}$ . Special attention was paid to avoid the sample bridging between the diamond culets [36]. Pressure was measured by the ruby fluorescence scale [37]. A home-built optical setup which consisted of a tungsten lamp, fused silica lenses, reflecting optics objectives (15x), and a visible-near-IR spectrometer (Ocean Optics Maya2000 Pro) was used to measure the optical absorption of the sample by using the sample-in, sample-out method, more detail can be found in earlier works [38,39].

### 2.2. Ab initio calculations

*Ab initio* total-energy calculations based on density functional theory (DFT) [40] for DC- $\text{CdGa}_2\text{S}_4$  and DC- $\text{HgGa}_2\text{S}_4$  were carried out with the Vienna *Ab initio* Simulation Package (VASP) [41]. The pseudopotential method and the projector-augmented wave (PAW) scheme [42] were used in order to include the full nodal character of the all electron charge density in the core region. The basis set of the plane waves was extended up to a reasonable energy cut off of 400 eV to achieve an accurate description of the electronic properties. The exchange-correlation energy was considered in the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof function for solids (PBEsol) prescription [43]. A dense special k-point sampling for the Brillouin zone (BZ) integration was used to have very well converged energies and forces. At selected volumes, the structures considered in this paper were fully relaxed to their optimized configuration through the calculation of the forces and the stress tensor, and it has been proved that relaxation of the structure has negligible effects on the electronic band structure based on comprehensive theoretical calculation studies of an OVC like  $\text{CdIn}_2\text{Se}_4$  [2]. In the optimized configurations, the forces on the atoms were less than  $0.0001 \text{ eV } \text{Å}^{-1}$ , and it is worthy of note that all the simulations were performed at zero temperature ( $T = 0 \text{ K}$ ). Electronic band structure



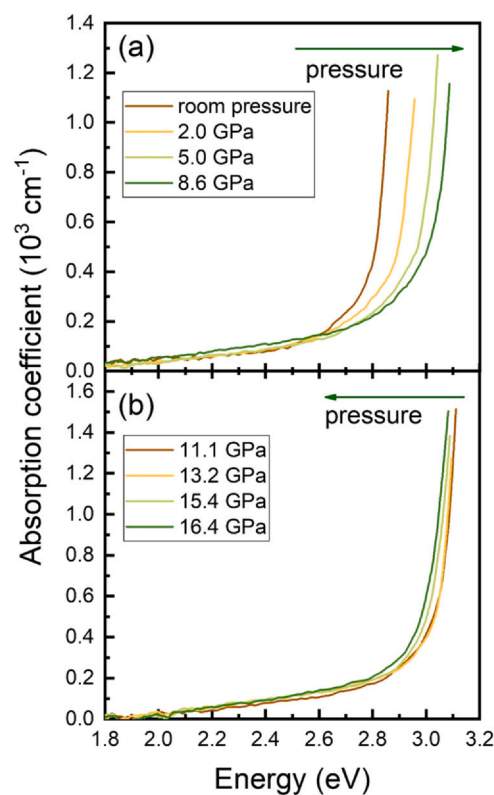
**Fig. 2.** Selected absorption edge of DC-CdGa<sub>2</sub>S<sub>4</sub> under compression (a) from ambient pressure to 8.1 GPa and (b) from 9.5 GPa to 16.4 GPa.

calculations were performed within the first BZ for both DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub>.

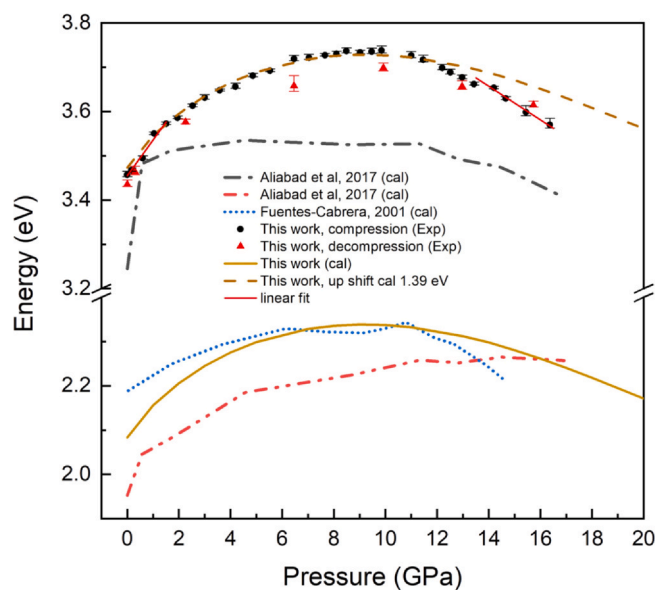
### 3. Results and discussion

The pressure dependence of the optical-absorption edge in DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub> are shown in Figs. 2 and 3, respectively. As regards DC-CdGa<sub>2</sub>S<sub>4</sub>, the absorption edge exhibits a blue-shift with increasing pressure up to 8.1 GPa. Then, a red-shift of the absorption edge occurs from 9.5 GPa to the highest pressure in this experiment (16.4 GPa). A similar behavior was also found in DC-CdGa<sub>2</sub>Se<sub>4</sub> [33]. In that compound, the optical-absorption edge first shows a blue-shift with increasing pressure up to 7.2 GPa and then a red-shift from 7.2 to 16 GPa [33]. As regards DC-HgGa<sub>2</sub>S<sub>4</sub>, its absorption edge first shows a blue-shift with increasing pressure up to 8.6 GPa, it keeps unchanged at the pressure interval from 8.6 to 11.1 GPa, and finally experiences a red-shift from 11.1 to 16.4 GPa. This behavior is similar to that described before for DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-CdGa<sub>2</sub>Se<sub>4</sub> and also similar to that already reported for DC-HgGa<sub>2</sub>Se<sub>4</sub> [33,44]. In that compound (DC-HgGa<sub>2</sub>Se<sub>4</sub>), the optical-absorption edge first shows a blue-shift with increasing pressure up to 11 GPa and then a red-shift above that pressure [33,44]. Therefore, our results show that the four Ga-based A<sup>II</sup>B<sub>2</sub><sup>III</sup>X<sub>4</sub><sup>VI</sup> OVCs, DC-CdGa<sub>2</sub>S<sub>4</sub>, DC-HgGa<sub>2</sub>S<sub>4</sub>, DC-CdGa<sub>2</sub>Se<sub>4</sub> and DC-HgGa<sub>2</sub>Se<sub>4</sub>, exhibit the same behavior of the optical absorption edge under compression irrespective of the A cation and X anion.

The low-energy tail, showing in the optical-absorption spectra in DC-CdGa<sub>2</sub>S<sub>4</sub> at 14.7 GPa and 16.4 GPa, can be caused by either a direct-to-indirect band gap crossover or by the light absorption due to pressure-induced defects in the samples [45]. Since our DFT calculations (see Figs. 4 and 5) do not predict any direct-to-indirect bandgap crossover either in DC-CdGa<sub>2</sub>S<sub>4</sub> or in DC-HgGa<sub>2</sub>S<sub>4</sub> up to 18 GPa, we ascribe the occurrence of the low-energy tail in DC-CdGa<sub>2</sub>S<sub>4</sub> at pressure above 14.7 GPa to pressure-induced defects that are precursors of a close pressure-induced phase transition which have been observed between 14 and 15 GPa in HP-RS measurements [22,25]. This explanation is similar to that already provided for



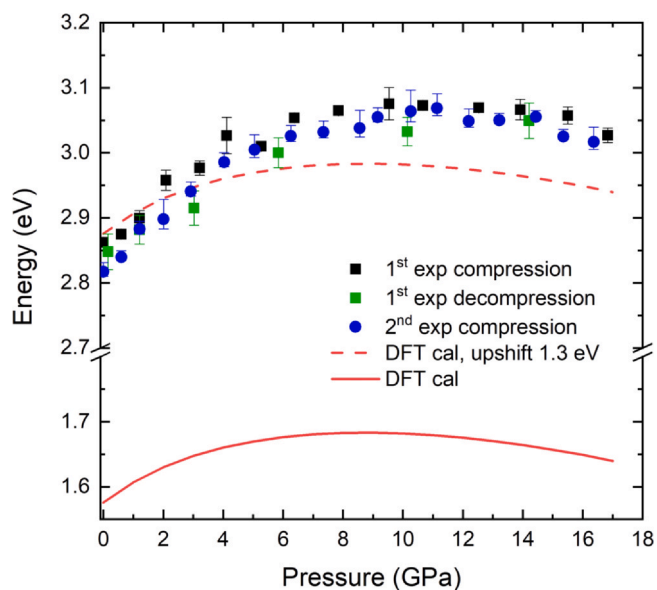
**Fig. 3.** Selected absorption edge of DC-HgGa<sub>2</sub>S<sub>4</sub> under compression (a) from room pressure to 8.6 GPa and (b) from 11.1 GPa to 16.4 GPa.



**Fig. 4.** Pressure dependence of the bandgap in DC-CdGa<sub>2</sub>S<sub>4</sub>. Experimental data (symbols) are compared to calculated data (lines). For comparison with our calculated data (yellow line), we have included the calculated data reported by Aliabad et al. (black line) [20,49], Aliabad et al. (red line) [20], and Fuentes-Cabrera (blue line) [23]. In order to better compare theoretical data with our experimental data, we have shifted our calculated data up by 1.39 eV (yellow dash line).

DC-HgGa<sub>2</sub>Se<sub>4</sub> [44], where the low-energy tail was found in the optical absorption spectra above 11.8 GPa, while the DFT calculations predicted a direct-to-indirect crossover above 16 GPa [33].

According to our calculations, the bandgap of DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub> is direct in good agreement with previous calculations (see Fig. S1 in Supplementary Materials) [3,46–49]. Actually, the



**Fig. 5.** Pressure dependence of the bandgap for DC-HgGa<sub>2</sub>S<sub>4</sub>. Experimental data (symbols) are compared to calculated data (lines). Calculated data have been upshifted by 1.3 eV to match the experimental data. Two independent optical absorption experiments were conducted to measure the pressure dependence of the bandgap and have been named as “1st exp” and “2nd exp”, respectively.

bandgaps of all  $A^{II}B_{2}^{III}X_{4}^{VI}$  compounds have been proven to be direct according to the literature [4]. Notably, we have plotted the theoretically derived crystal structural parameters and unit-cell volume of DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub> as a function of pressure alongside the reported experimental and DFT calculated data (see Supplementary Materials, Figs. S2-S5) [21,31] and the stability of the crystal structure have been well-checked in our calculation [50–52]. A good agreement between theory and experiment is achieved, thus demonstrating that our DFT calculations provide a proper description on the equation of state of those two materials under pressure and enable us to get a more comprehensive understanding of the effect of pressure on the electronic band structure of the two OVCs.

By using the Tauc plot for direct bandgap materials [53], we have extrapolated the linear fit of the high-energy part of the  $(\alpha h\nu)^2$  vs  $h\nu$  plot to zero, where  $\alpha$  is the absorption coefficient,  $h$  is Planck's constant and  $\nu$  is the photon's frequency, to obtain the direct bandgap of DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub> at different pressures (see Figs. 4 and 5). At normal pressure, the bandgap of DC-CdGa<sub>2</sub>S<sub>4</sub> is 3.46 eV, in excellent agreement with the previous experimental optical absorption data (3.44 eV) [19]. Our ab initio GGA-PBESol calculations yield an underestimated direct bandgap of 2.10 eV that agrees with previous theoretical calculations (2.20 eV [47], 2.12 eV [54] and 2.19 eV [55]). For DC-HgGa<sub>2</sub>S<sub>4</sub>, the average experimental direct bandgap obtained at ambient pressure from two experiments is 2.84(2) eV, which compares with the underestimated value of 1.58 eV in our theoretical calculations. These values are consistent with the values obtained by earlier experiments (2.84 eV) [28,29] and calculations (1.57 eV) [4], respectively.

Although it is well known that DFT calculations usually underestimate the bandgap and the different exchange-correlation functional provide different values for the bandgap, we will see in the next section that our GGA-PBESol calculations indeed provide a good description of the pressure dependence of the bandgap for the two OVCs. This will enable us to understand how pressure affects their electronic band structures.

The experimental and theoretical pressure dependence of the bandgap for DC-CdGa<sub>2</sub>S<sub>4</sub> obtained from the optical absorption edge by the Tauc plot method and our DFT calculations, respectively, is

shown in Fig. 4. In addition, theoretical results from the literature have been also added for comparison. As observed, both our experimental and theoretical results agree up to 12 GPa if we upshift the calculated data by 1.39 eV, so as to bring into coincidence both experimental and theoretical bandgap values at 0 GPa. They also show a strong nonlinear dependence of the direct band gap of DC-CdGa<sub>2</sub>S<sub>4</sub>. Curiously, we have observed that DFT calculations with different exchange correlation potentials give different results on the same material. Aliabad et al. provided the calculated electronic band structure for DC-CdGa<sub>2</sub>S<sub>4</sub> by adopting GGA (red line) and mBJ (black line) functionals [20,49]. None of them exhibit the same nonlinear pressure dependence of the bandgap as in our experiments. The bandgap calculated by the mBJ equation is indeed closer to the experimental value, but it shows a big jump at low pressures and becomes less nonlinear under pressure than the experimental values in the whole pressure range. On the other hand, the pressure dependence of the bandgap obtained with LDA functional by Fuentes-Cabrera [41,42] is much closer to our calculated and experimental results, except for the odd decrease of the bandgap within the intervals 6.1–10.8 GPa and the higher pressure coefficient of the bandgap above 10.8 GPa when compared with our optical-absorption experiment determined bandgap of DC-CdGa<sub>2</sub>S<sub>4</sub>, in which the bandgap increases continuously from ambient pressure up to 8.4 GPa and decrease from 10 GPa to the highest pressure. These features are in good agreement with our DFT calculations. In summary, the good agreement between our experimental and theoretical calculations gives us confidence to learn about the microscopic origin of the nonlinear pressure dependence of the direct bandgap in DC-CdGa<sub>2</sub>S<sub>4</sub>.

It can be noted that the agreement between our experimental and theoretical data for the direct bandgap of DC-CdGa<sub>2</sub>S<sub>4</sub> is worst above 12 GPa, the experimental values are much lower than the theoretical ones. Two reasons may be the cause for this discrepancy: i) The onset of the non-hydrostaticity in our experiments induced by deterioration of the PTM used in our experiment (4:1 methanol: ethanol mixture) above the known hydrostatic limit [56,57]; ii) A partial order-disorder transition occurring in our experiment, prior to the DC-DR transition, as already observed from the absorption spectra of DC-CdGa<sub>2</sub>S<sub>4</sub> at pressure above 14.7 GPa and reported in previous HP studies of DC-CdGa<sub>2</sub>S<sub>4</sub> [21,22,24,25]. This disorder is not considered in our calculations since the position of the cations and vacancies are fixed in the DC structure of CdGa<sub>2</sub>S<sub>4</sub>.

We think that the cause for the decrease of the direct bandgap in DC-CdGa<sub>2</sub>S<sub>4</sub> is related to an order-disorder process and not related to the deterioration of hydrostatic environment. As we have mentioned in the introduction, HP-RS measurements in several OVCs indeed have found the onset of the order-disorder stage in DC-CdGa<sub>2</sub>S<sub>4</sub> around 10 GPa [22,24,25]. Moreover, the decreasing bandgap caused by increasing cation-vacancy disorder at HP has been discussed and proven in a previous optical study of other  $AB_2X_4$  OVC, like DC-HgGa<sub>2</sub>Se<sub>4</sub> [44]. In this context, we must mention that the bandgap of DC-CdGa<sub>2</sub>S<sub>4</sub> collected in the decompression process from 16.8 GPa provide evidence that the change of the bandgap is almost reversible in our experiment, thus suggesting that the order-disorder stage is almost reversible in this pressure range, despite at several pressures the estimated bandgap on downstroke is slightly smaller than on upstroke. Indeed, the highest pressure (16.4 GPa) achieved in our HP optical absorption measurements on DC-CdGa<sub>2</sub>S<sub>4</sub> is not enough to make the DC-to-DR transition irreversible based on the HP-XRD experiment [21].

Similarly, the experimental and theoretical pressure dependence of the bandgap for DC-HgGa<sub>2</sub>S<sub>4</sub> obtained from the optical-absorption edge by the Tauc plot and from DFT calculations, respectively, is shown in Fig. 5. Here we report two independent optical absorption experiments on DC-HgGa<sub>2</sub>S<sub>4</sub>, and the bandgap, from both experiments, indeed shows a good agreement not only in the pressure

coefficient but also value. We also upshift the calculated bandgap by 1.3 eV to better compare with the experimental data. The agreement between the experimental and calculated bandgap is good after the upshifting despite the small discrepancy at the pressure above 6 GPa. Again, both the experimental and theoretical data show a nonlinear pressure dependence of the direct bandgap of DC-HgGa<sub>2</sub>S<sub>4</sub>. Besides, the bandgap collected in the decompression process of the 1st experiment indicated a reversible change of the bandgap of DC-HgGa<sub>2</sub>S<sub>4</sub> under compression, which is understandable since the highest pressure in our two experiments (17.4 GPa and 16.4 GPa) are below the onset of order-disorder phase transition found in a previous HP-RS experiment (18 GPa) [30]. Therefore, we can conclude here that the experimental and calculated bandgaps for DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub> at high pressure confirm that the nonlinear pressure dependence of the bandgap is a general feature of adamantite OVCs. This conclusion is in agreement with the published literature for other OVCs (DC-CdGa<sub>2</sub>Se<sub>4</sub> and DC-HgGa<sub>2</sub>Se<sub>4</sub> in Ref. [33,44], Ga<sub>2</sub>Se<sub>3</sub> [34], Ga<sub>2</sub>S<sub>3</sub> [35]). Moreover, our present results allow us to conclude that the nonlinear pressure dependence of the band gap in adamantite OVCs does not depend on the cations or anions present in their formula unit [33].

We have summarized in Table 1 the experimental and theoretical pressure coefficients obtained for DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub>, by adopting a linear fit on the bandgap at pressures below 3 GPa and at pressures above 14 GPa. Experimental results for DC-CdGa<sub>2</sub>Se<sub>4</sub> and DC-HgGa<sub>2</sub>Se<sub>4</sub> [33,44] are also shown for comparison. In the upstroke process of DC-CdGa<sub>2</sub>S<sub>4</sub>, both the experiment and calculation show a high zero-pressure pressure coefficient of the direct bandgap, which is more than two times larger than that of DC-CdGa<sub>2</sub>Se<sub>4</sub> [33] derived from the experimental data. Moreover, this value is higher than those of other reported OVCs, like DC-HgGa<sub>2</sub>Se<sub>4</sub> [33,44], DC-MnGa<sub>2</sub>Se<sub>4</sub> [58], β-Ga<sub>2</sub>Se<sub>3</sub> [34], zincblende and wurtzite CdSe [59,60] and DC-HgGa<sub>2</sub>S<sub>4</sub>. Therefore, the zero-pressure pressure coefficient of DC-CdGa<sub>2</sub>S<sub>4</sub> is the highest one among the reported OVCs to our knowledge. On the other hand, the experimental zero-pressure pressure coefficient of the direct bandgap of DC-HgGa<sub>2</sub>S<sub>4</sub> is a little higher than that of DC-HgGa<sub>2</sub>Se<sub>4</sub> reported in both Ref. [33,44]. The same conclusions can be drawn for the experimental high-pressure pressure coefficients above 14 GPa. The negative slope in DC-CdGa<sub>2</sub>S<sub>4</sub> is higher than in the rest of OVCs. Those trends are confirmed by theoretical calculations. We have found that the negative experimental high-pressure pressure coefficients above 14 GPa are higher in absolute value than those of calculations on both DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub>. A similar behavior has been observed in DC-CdGa<sub>2</sub>Se<sub>4</sub> and DC-HgGa<sub>2</sub>Se<sub>4</sub> [33]. This trend suggests that there are two factors that cause the nonlinear behavior of the direct bandgap under compression in those two OVCs: i) the change of the electronic band structure under compression as the calculation results shown and ii) the increasing disorder under compression which have not been simulated in our calculation but observed in other OVCs [44]. The first one, we will discuss it later, is caused by a band anticrossing (BAC) and occurs in all OVCs between 8 and 12 GPa [33,35]. The second one is related to a pressure-induced

cation-vacancy disorder and usually occurs above the same pressure range as the BAC [44].

Now, we will analyze the electronic band structure and related crystal structure change of DC-CdGa<sub>2</sub>S<sub>4</sub> as an example to reveal the reason of the strong nonlinear bandgap change found in the two sulfur-based OVCs. Fig. 6a shows the pressure dependence of the theoretical energy of the valence band maximum (VBM) and the three lowest conduction bands (CBs) at the  $\Gamma$  point. All of them have been fitted by quadratic functions. The lowest CB at  $\Gamma$  point is called 1st CB or conduction band minimum (CBM), while the other two are called 2nd and 3rd CBs. The evolution of the pressure coefficients of the VBM and CBM with increasing pressure are also reported in Fig. 6b. We can observe that both pressure coefficients decrease at HP. Below 10 GPa, the pressure coefficient of the VBM is lower than that of CBM, resulting in a broadening of the bandgap. Above 10 GPa, the pressure coefficient of the VBM is higher than that of CBM, resulting in a narrowing of the bandgap, the reason of the change on the pressure coefficient can be found later. In summary, the strong pressure dependence of the VBM (with a pressure coefficient comparable to that of the CBM) and the strong decrease of the pressure coefficient of the CBM above 10 GPa cause the strong nonlinear dependence of the direct bandgap. In fact, the strong decrease of the pressure coefficient of the CBM is caused by the BAC of two conduction bands [61]. In the case of DC-CdGa<sub>2</sub>S<sub>4</sub>, the BAC occurs around 14 GPa between the CBM and 3rd CB (see Fig. 6c). Notably, the BAC happened between the CBM and 3rd CB according to the ordering of bands at room pressure (see Fig. 6a), unlike in other OVCs where the BAC usually occurs between the CBM and the 2nd CB. The reason for this difference is because in DC-CdGa<sub>2</sub>S<sub>4</sub> the 3rd CB at room pressure becomes the 2nd CB above 5 GPa (see Fig. 6a). This crossing of the 2nd and 3rd CBs at HP is characteristic of DC-CdGa<sub>2</sub>S<sub>4</sub> and has not been reported in other OVCs.

In order to better understand the BAC, we only plot in Fig. 6c the pressure dependence of the calculated energy of the 1st and 3rd CBs (symbols), as well as the expected pressure dependence (in a tentative way) of both bands in the absence of BAC (lines). The strong change of the pressure coefficient of the direct bandgap as a consequence of the strong change of the pressure coefficient of the CBM above 10 GPa is the first evidence of the BAC. A similar BAC has been observed in other OVCs, including DC-CdGa<sub>2</sub>Se<sub>4</sub>, DC-HgGa<sub>2</sub>Se<sub>4</sub>, β-Ga<sub>2</sub>Se<sub>3</sub> [33], and α'-Ga<sub>2</sub>S<sub>3</sub> [35]. More evidence of the BAC between the 1st and 3rd CB can be found in the totally reversed atomic character showed by both bands between room pressure and high pressure close to 20 GPa (Fig. 6d and e) to be discussed below.

In order to understand the pressure coefficients of the different electronic bands, we need to know the atomic characters of the different bands in DC-CdGa<sub>2</sub>S<sub>4</sub> in a similar way to other OVCs, like CdIn<sub>2</sub>Se<sub>4</sub> [2]. For that purpose, we can treat the bonding in DC-CdGa<sub>2</sub>S<sub>4</sub> by a simple valence-bond model. Due to the ordered vacancy occupying the 2d Wyckoff position, each S in DC-CdGa<sub>2</sub>S<sub>4</sub> only bonds with two Ga in 2a and 2b position and one Cd by donating 5/4 electrons to Ga-S bond and 6/4 electrons to Cd-S bonds. Therefore, S atoms show a p-type bonding leaving two s electrons as a lone

**Table 1**

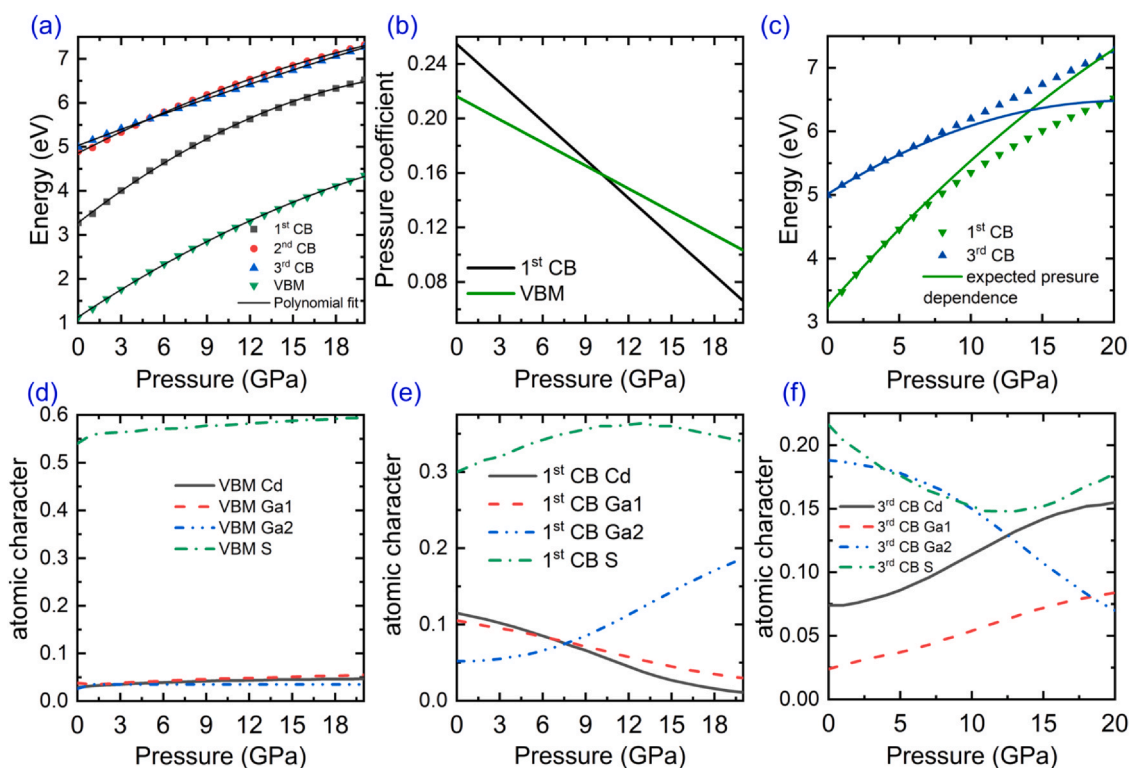
Summary of the experimental (Exp.) and theoretical (DFT) zero-pressure and high-pressure pressure coefficients ( $dE/dP$ , in meV/GPa) of the bandgap of DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub>, by adopting a linear fit on the bandgap at pressures below 3 GPa and at pressures above 14 GPa. Experimental and theoretical results for DC-CdGa<sub>2</sub>Se<sub>4</sub> and DC-HgGa<sub>2</sub>Se<sub>4</sub> obtained from fits of data of Refs. [33,44] using the same method are also shown for comparison.

Compound	Exp. zero-pressure $dE/dP$	DFT. zero-pressure $dE/dP$	Exp. high-pressure $dE/dP$	DFT. high-pressure $dE/dP$
DC-CdGa <sub>2</sub> S <sub>4</sub>	81 ± 6	72	-38 ± 3	-23
DC-CdGa <sub>2</sub> Se <sub>4</sub>	36 ± 4 <sup>a</sup>	34 <sup>a</sup>	-11 ± 3 <sup>a</sup>	-8 <sup>a</sup>
DC-HgGa <sub>2</sub> S <sub>4</sub>	39 ± 4 <sup>c</sup> or 42 ± 4 <sup>d</sup>	27	-13 ± 5 <sup>c</sup> or -20 ± 7 <sup>d</sup>	-8
DC-HgGa <sub>2</sub> Se <sub>4</sub>	31 ± 3 <sup>a</sup> or 31 ± 4 <sup>b</sup>	30 <sup>a</sup>	-7 ± 2 <sup>a</sup> or -20 ± 3 <sup>b</sup>	-1 <sup>a</sup>

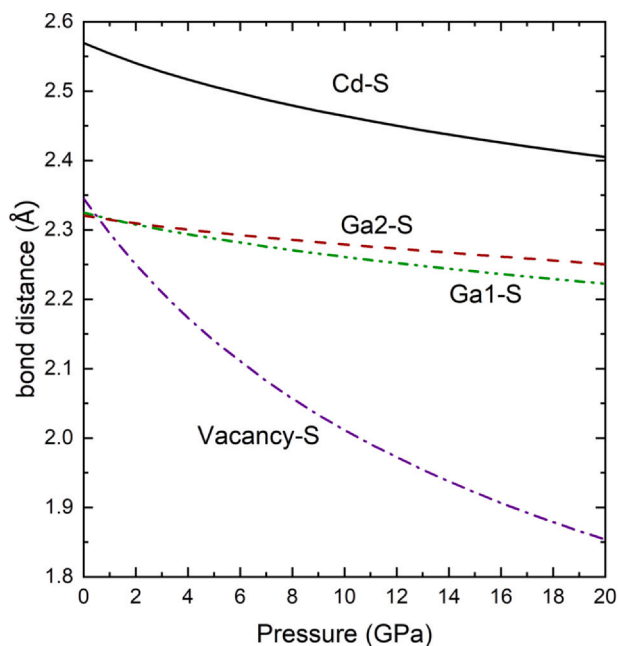
<sup>c, d</sup>The first and second optical absorption experiment on DC-HgGa<sub>2</sub>S<sub>4</sub> in this work.

<sup>a</sup> Reference [33].

<sup>b</sup> Reference [44].



**Fig. 6.** Summary of the theoretically calculated electronic band structure of DC-CdGa<sub>2</sub>S<sub>4</sub>. (a) symbols are the calculated energy of the valence band maxima (VBM) and three lowest conduction band (1st, 2nd and 3rd CB, the sequence is determined at 0 GPa) at the  $\Gamma$  point as a function of pressure. The solid line is the polynomial fit to the calculated energy employing the quadratic function:  $E(P) = C + AP + BP^2$ . (b) pressure coefficient of the VBM and 1st CB derived from the quadratic equation determined from the fitting in (a). (c) calculated pressure dependence (symbols) of the energy of the 1st CB and 3rd CB at  $\Gamma$  point. The solid lines show the expected pressure dependence of both CB energies in absence of band anticrossing. (d)–(f) are the theoretically predicted atomic contribution to the energy of VBM, 1st and 3rd CB at  $\Gamma$  point as a function of pressure, respectively. Additionally, Ga1 correspond to the Ga in 2b Wyckoff position while Ga2 is the Ga in 2c Wyckoff position, which is illustrated in Fig. 1.



**Fig. 7.** Theoretical calculated pressure dependence of the bond distances in DC-CdGa<sub>2</sub>S<sub>4</sub>. Ga1 correspond to the Ga in 2b Wyckoff position while Ga2 is the Ga in 2c Wyckoff position, which is illustrated in Fig. 1.

electron pair (LEP) since the valence configuration is  $3s^23p^4$  for S, this feature also can be observed in the electron localization function (ELF) of DC-CdGa<sub>2</sub>S<sub>4</sub> in Fig. S6 in Supplementary Material. Also,

theoretical calculations predict that the VBM is mainly dominated by the s orbital of S with negligible contribution from any other atoms (Fig. 6d), indicating that the VBM is mainly contributed by non-bonding LEP orbital rather than by any bond between anion and cation. Consequently, the stronger pressure dependences of the VBM under pressure is likely because of the strong repulsion between the LEP orbits in neighbor S as a result of the strong compressibility of the S-vacancy distance (Fig. 7). On the other hand, the strong pressure dependence of the CBM at low pressures is given by the high s cation (Cd and Ga1) contribution (Fig. 6e), this information also has been well characterized by the electronic density of state (DOS) and projected density of state (PDOS) of DC-CdGa<sub>2</sub>S<sub>4</sub> at 0 GPa which can be found in Fig. S7 in Supplementary Material, since it is well known that non-bonding s cation levels give rise to strong pressure coefficients of the CBM due to the strong repulsion between bonding and non-bonding cation s levels. In this context, the small pressure coefficient of the 3rd CB at low pressures can be ascribed to the high Ga2 contribution but small Cd and Ga1, as well as S, contributions (Fig. 6f) due to the smaller compression of the Ga2-S bond than of the Cd-S and Ga1-S bonds along the whole pressure range in Fig. 7.

Evidence of the BAC between the two CBs near 14 GPa can be observed in the totally reversed change of the atomic character between the 1st CB and 3rd CB between low pressures and high pressures close to 20 GPa (Fig. 6e and f). While there is almost no change in the atomic character (s orbital of S) of the VBM in the whole pressure range (Fig. 6d), a considerable change of the atomic character of the 1st CB and 3rd CB occurs at HP (Fig. 6e and f). As already commented, at low pressures the CBM was dominated by the s and p orbital of S, with small contribution from the s orbital of Cd and Ga1 (Ga at 2b Wyckoff position) and minor contribution from

s orbital of Ga2 (Ga at 2c Wyckoff position). In contrast, the 3rd CB is mainly contributed by the s character of S and Ga2, a small contribution from s character of Cd and a minor contribution from s character of Ga1. At high pressures close to 20 GPa, both bands reverse their atomic characters; a characteristic feature of a BAC.

For DC-HgGa<sub>2</sub>S<sub>4</sub>, the strong nonlinear pressure dependence of the direct bandgap at the  $\Gamma$  point can be explained in a similar way as for DC-CdGa<sub>2</sub>S<sub>4</sub>. In DC-HgGa<sub>2</sub>S<sub>4</sub> there is a BAC around 13 GPa between the 1st and 2nd CB (see Fig. S8 in the Supplementary Material). As expected, the BAC is evidenced by the reversed atomic character change between first and second lowest CB at zero pressure (see Figs. S9 and S10 in the Supplementary Material).

#### 4. Conclusions

In summary, we have investigated the band structure of two sulfur-based adamantine ordered-vacancy compounds, CdGa<sub>2</sub>S<sub>4</sub> and HgGa<sub>2</sub>S<sub>4</sub>, employing optical-absorption experiments and DFT calculations at HP. We have found that DC-CdGa<sub>2</sub>S<sub>4</sub> shows the strongest zero-pressure pressure coefficient of the direct bandgap of all known ordered-vacancy compounds. The strong nonlinear pressure dependence of the direct bandgap of both compounds, found both in experiments and theoretical calculations, provides conclusive support to the claim of the common nonlinear pressure dependence of the bandgap in all adamantine ordered-vacancy compounds, as already reported [33].

Thanks to the analysis of the calculated electronic band structure of the two compounds, we have found that the nonlinear behavior of the direct bandgap is caused by the band anticrossing between the 1st and the 3rd CB in DC-CdGa<sub>2</sub>S<sub>4</sub> and between 1st and the 2nd CB in DC-HgGa<sub>2</sub>S<sub>4</sub>, according to the ordering of bands at room pressure. Since the band anticrossing has been usually found to occur between the 1st and the 2nd CBs in Se-based ordered-vacancy compounds with smaller bandgaps than S-based ones, perhaps a band anticrossing between the 1st and 3rd CB could also occur in DC-ZnGa<sub>2</sub>S<sub>4</sub> with a direct bandgap (3.18 eV [62]); i.e. in those of DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub>.

We have also confirmed that the strong pressure dependence of the topmost valence band of ordered-vacancy compounds largely depends on the anion lone electron pair pointing to the cation vacancy. Furthermore, we have attributed the higher bandgap narrowing in experiment above 10 GPa compared to that in calculation in both compounds to a partial pressure-induced order-disorder transition, which occurs prior to the phase transition to the disordered rocksalt structure. The bandgap changes of both DC-CdGa<sub>2</sub>S<sub>4</sub> and DC-HgGa<sub>2</sub>S<sub>4</sub> under pressure up to around 17 GPa was found to be reversible. Both the strong bandgap narrowing and reversibility from 17 GPa are similar to those previously found in selenium-based ordered-vacancy compounds. Therefore, our results confirm that pressure-induced order-disorder processes are common to all ordered-vacancy compounds irrespective of the anion.

#### CRediT authorship contribution statement

**A. Liang:** Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **L. T. Shi:** Data curation, Formal analysis. **S. Gallego-Parra:** Formal analysis, Writing – review & editing. **O. Gomis:** Formal analysis, Writing – review & editing. **D. Errandonea:** Formal analysis, Funding acquisition, Supervision, Writing – review & editing. **I. M. Tiginyanu:** Methodology, Writing – review & editing. **V. V. Ursaki:** Methodology, Writing – review & editing. **F. J. Manjón:** Formal analysis, Writing – original draft, Funding acquisition, Supervision.

#### 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.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.161226.

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