Nonlinear pressure dependence of the direct band gap in adamantine ordered-vacancy compounds

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A strong nonlinear pressure dependence of the optical absorption edge has been measured in defect chalcopyrites $CdGa_2Se_4$ and $HgGa_2Se_4$. The behavior is due to the nonlinear pressure dependence of the direct band-gap energy in these compounds as confirmed by *ab initio* calculations. Our calculations for $CdGa_2Se_4$, $HgGa_2Se_4$ and monoclinic β-Ga_2Se_3 provide evidence that the nonlinear pressure dependence of the direct band-gap energy is a general feature of adamantine ordered-vacancy compounds irrespective of their composition and crystalline structure. The nonlinear behavior is due to a conduction band anticrossing at the Γ point of the Brillouin zone caused by the presence of ordered vacancies in the unit cell of these tetrahedrally coordinated compounds.

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I. INTRODUCTION

Adamantine compounds are tetrahedrally coordinated materials whose structure derives from the cubic diamond structure. They include binary zincblende compounds and their alloys and ternary compounds like chalcopyrite, stannite, and famatinite. A different kind of adamantine compounds are ordered-vacancy compounds (OVCs), in which a cationic site at the unit cell is vacant in an ordered and stoichiometric fashion. Adamantine OVCs include binary $B_2^{III}X_3^{VI}$ and ternary $A^{II}B_2^{III}X_4^{VI}$ compounds, in which one third and one fourth of the cation sites are vacant, respectively. OVCs crystallize in noncubic structures because the presence of several nonequivalent tetrahedrally coordinated cations produces a distortion of the crystal lattice from the cubic symmetry. The lack of cubic symmetry of OVCs provides them with special properties with important applications in optoelectronics, solar cells, and nonlinear optics that have attracted considerable attention.[1–3] Furthermore, they are important materials in solid state physics and defect engineering from a fundamental point of view because they can help to understand the role played by vacancies in the physical and chemical properties of solids. Note that OVCs constitute a bridge between common materials (with vacancies as point or line defects) and amorphous or defect materials (with vacancies and other defects preventing long-range order).

Ternary $A^{II}B_2^{III}X_4^{VI}$ compounds crystallize in the defect chalcopyrite (DC, $I\bar{4}$), defect stannite (DS, $I\bar{4}2m$), or pseudocubic (PS, $P\bar{4}2m$) structures.[1,2] Figure 1(a) shows the tetragonal DC structure of cadmium digallium selenide ($CdGa_2Se_4$) whose atoms (Wyckoff site) are Ga (2a), vacancy (2b), Ga (2c), Cd (2d), and Se (8g) and Fig. 1(b) shows the pseudocubic PS structure of $CdGa_2Se_4$. Theoretical calculations of the optical band-gap energies at different pressures in some ternary OVCs with DC structure have been reported;[3–5] however, only a couple of measurements on the pressure dependence of the optical absorption in OVCs [DC-$MnGa_2Se_4$ (Ref. 6) and monoclinic β-Ga_2Se_3 (Ref. 7)] have been reported. In this work, we report high-pressure optical absorption measurements in DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$ and first-principles calculations of the electronic structure for these compounds, and for β-Ga_2Se_3 whose monoclinic Cc structure is shown in Fig. 1(c). We will show that adamatine OVCs exhibit strikingly large absolute deformation potentials for the valence and conduction bands, which are up to 10 times larger than those in tetrahedral semiconductors with zincblende or wurtzite structures. Furthermore, we will show that they have a strong nonlinear pressure dependence of the direct band gap caused by: (i) a large pressure coefficient of the topmost valence band (VB), and (ii) a band anticrossing of the two lowermost conduction bands (CBs) at high pressure.

II. EXPERIMENTAL DETAILS

Stoichiometric single crystals of DC-$CdGa_2Se_4$ (DC-$HgGa_2Se_4$) around 20 μm in thickness and grown from its constituents CdSe (HgSe) and Ga_2Se_3 by chemical vapor

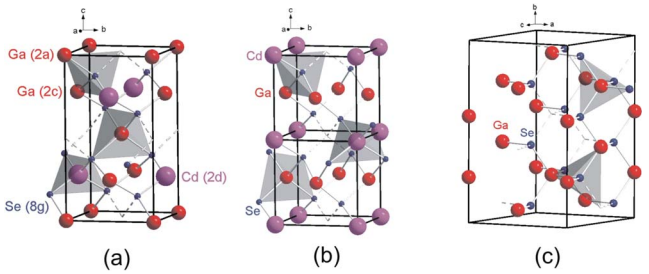

FIG. 1. (Color online) Structure of the defect chalcopyrite (a) (DC) $CdGa_2Se_4$, (b) pseudocubic (PS) $CdGa_2Se_4$, and (c) β-Ga_2Se_3. Big light atoms are Cd, medium dark atoms are Ga, and small dark atoms are Se. To distinguish between nonequivalent atoms in the DC structure the Wyckoff sites relevant for the discussion of Fig. 6 are given in parenthesis. The DC- and PS-$HgGa_2Se_4$ structures are obtained by substituting Cd atoms by Hg atoms in the (a) and (b) pictures.

transport method,[8] were loaded together with a 16:3:1 methanol-ethanol-water mixture and a ruby chip for pressure calibration in a diamond anvil cell. High-pressure absorption experiments at room temperature were performed with a micro-optical system[9] up to 16 GPa, pressure at which the samples become opaque due to the transition to the disordered rocksalt phase.[10]

III. *AB INITIO* CALCULATIONS

Ab initio total energy and electronic structure calculations in $CdGa_2Se_4$ and $HgGa_2Se_4$ were performed both for the real DC structure and a hypothetical PS structure, and for β-Ga_2Se_3 with monoclinic Cc structure[7] within the framework of the pseudopotential method and the density functional theory with the VASP code.[11] The exchange and correlation energy was taken in the generalized gradient approximation according to Perdew-Burke-Ernzerhof prescription[12] in order to give account for the large charge density fluctuations around vacancies. The projector-augmented wave scheme[13] was adopted and the semicore $4d$ ($5d$) electrons of Cd (Hg), and $3d$ electrons of Ga atoms were dealt with explicitly. Kinetic energy cutoff and k-point mesh were used for Brillouin-zone integrations ensuring energy convergence to about 1 meV per formula unit. The values used for kinetic energy cutoff and k-points number are shown in Table I. At each volume, the structures were fully relaxed to their equilibrium configuration, with forces smaller than 0.002 eV/Å and a negligible deviation of the stress tensor from a diagonal hydrostatic form.

TABLE I. Kinetic energy cutoff and k-points number for β-Ga_2Se_3 and for DC- and PS-$CdGa_2Se_4$ and $HgGa_2Se_4$.

	E_{cutoff} (eV)	k-points number
DC-$CdGa_2Se_4$	400	40
DC-$HgGa_2Se_4$	400	36
β-Ga_2Se_3	380	20
PS-$CdGa_2Se_4$	400	18
PS-$HgGa_2Se_4$	550	30

Table II shows the calculated and experimental lattice parameters, volume, bulk modulus, and pressure derivative of the bulk modulus for β-Ga_2Se_3, for DC- and PS-$CdGa_2Se_4$ and for DC and PS-$HgGa_2Se_4$ at room pressure. Agreement between calculated and experimental structural parameters at room pressure for DC-$CdGa_2Se_4$, DC-$HgGa_2Se_4$, and β-Ga_2Se_3 give us confidence about the accuracy of the calculated pressure dependence of the electronic band structures. Theoretical and experimental deviations of the lattice parameters and volume of the reported compounds are within the error margins of experiments and calculations. However, there is a large deviation between the experimental and theoretical bulk modulus of DC-$CdGa_2Se_4$ and β-Ga_2Se_3 (around 25%). We think that the explanation for the disagree-

TABLE II. Calculated and experimental lattice parameters, volume, bulk modulus, and bulk modulus pressure coefficient for β-Ga_2Se_3 and for DC and PS-$CdGa_2Se_4$ and $HgGa_2Se_4$ at room pressure. All calculations have been performed within the generalized gradient approximation except those for β-Ga_2Se_3 which are made within the local gradient approximation.

		a (Å)	b (Å)	c (Å)	V_0 (Å^3)	B_0 (GPa)	B_0'
DC-$CdGa_2Se_4$	Theoretical	5.843	5.843	11.075	378.04	31.6	4.5
	Experimental[a]	5.743	5.743	10.756	354.80	41.5	5.0
DC-$HgGa_2Se_4$	Theoretical	5.872	5.872	11.008	379.56	30.8	4.8
	Experimental[b]	5.693	5.693	10.826	350.87		
β-Ga_2Se_3	Theoretical	6.556	11.484	6.561	467.52	39.9	4.7
	Experimental	6.661[c]	11.652[c]	6.649[c]	488.38[c]	51.0[d]	
PS-$CdGa_2Se_4$	Theoretical	5.565	5.565	6.054	187.48	35.8	4.0
PS-$HgGa_2Se_4$	Theoretical	5.575	5.575	6.125	190.35	34.7	4.2

[a]Reference 10.
[b]Reference 15.
[c]Reference 16.
[d]Reference 14.

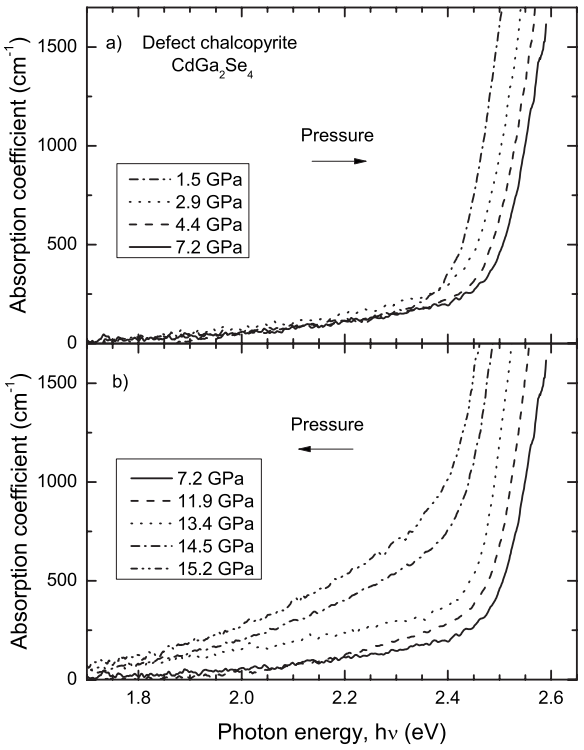

FIG. 2. Absorption edge of defect chalcopyrite $CdGa_2Se_4$ on increasing pressure up to (a) 7.2 GPa and from 7.2 up to (b) 16 GPa.

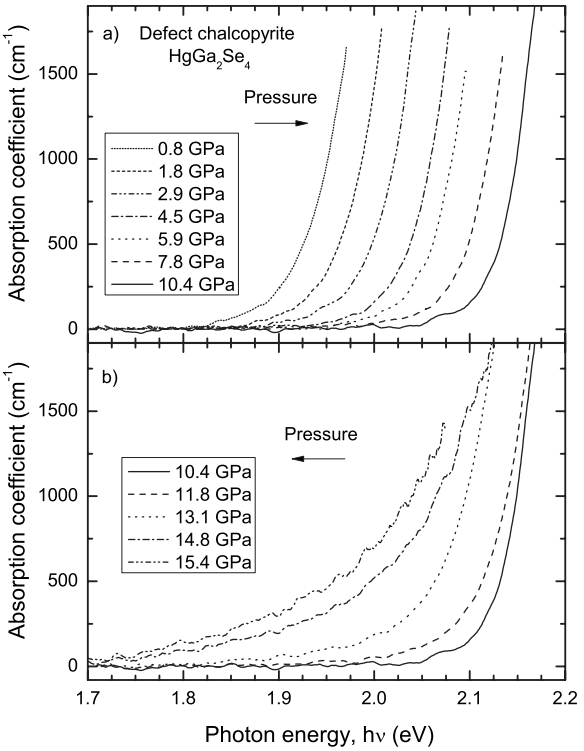

FIG. 3. Absorption edge of defect chalcopyrite $HgGa_2Se_4$ on increasing pressure up to (a) 10.4 GPa and (b) from 10.4 up to 15.4 GPa.

ment is on one hand the slightly underestimation of the bulk modulus in the calculations and, on the other hand, a possible overestimation of the experimental bulk modulus in Refs. 10 and 14. Note that the experimental values of the bulk modulus and its pressure derivative depend on the number of data fitted, the pressure range covered, and the equation of state used. No explanation regarding the data points fitted neither the equation of state used is given in Ref. 14. On the other hand, authors of Ref. 10 obtained the equation of state by fitting data only up to 7 GPa (8 points in total) and not up to 14 GPa like in our calculations (just prior to the phase transition toward the disordered rocksalt phase). In addition, the authors of Ref. 10 used a Murnaghan equation of state to fit the experimental data instead of the Birch-Murnaghan equation of state used in theoretical calculations. A similar reasoning can explain the difference between theoretical and experimental data of the bulk modulus of β-Ga_2Se_3.

IV. RESULTS AND DISCUSSION

Figure 2 shows the pressure dependence of the optical absorption spectra in DC-$CdGa_2Se_4$. In the case of DC-$CdGa_2Se_4$ the absorption edge exhibits a blue shift with increasing pressure up to 7.2 GPa and a red shift from 7.2 to 16 GPa. The high value of the absorption coefficient, α, its steep increase with photon energy, $h\nu$, and the linear character of the $(\alpha h\nu)^2$ vs $h\nu$ plot at high energies (not shown), are indicative of the direct allowed nature of the band gap in DC-$CdGa_2Se_4$, in agreement with our calculations and with Refs. 6 and 17. The pressure dependence of the absorption spectra for DC-$HgGa_2Se_4$ is reported in Fig. 3. The optical absorption edge in DC-$HgGa_2Se_4$ has a similar evolution than in DC-$CdGa_2Se_4$ showing a blue shift with increasing pressure up to 10.4 GPa and afterwards a red shift up to the phase transition around 15 GPa.

Figures 4(a) and 4(b) show the pressure dependence of the direct band-gap energy in DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$, respectively, obtained by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ vs $h\nu$ plot to zero absorption. For DC-$CdGa_2Se_4$, the experimental direct band-gap energy at room pressure (2.40 eV) agrees with previous measurements,[17] while the theoretical value (1.34 eV) is in agreement with earlier calculations.[3,5] For DC-$HgGa_2Se_4$, we obtain an experimental (calculated) direct band gap of 1.93 eV (0.92 eV) at room pressure. Despite more accurate values of the direct band gaps can be obtained at higher absorption coefficients than 1500 cm^{-1} using thinner samples,[7] we have obtained a rather accurate pressure dependence of the direct band-gap energy as judged by the good agreement between the experimental and theoretical data at low pressures shown in Fig. 4. The absorption region up to 1500 cm^{-1} allows also to check the direct nature of the fundamental band gap and the appearance of any indirect edge on increasing pressure. Our measurements and calculations discard the appearance of any indirect edge below the direct one in DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$ upon compression. The appearance of an energy tail at pressures above 11 GPa is ascribed to light scattering caused by point defects previous to the phase transition toward the disordered rock-

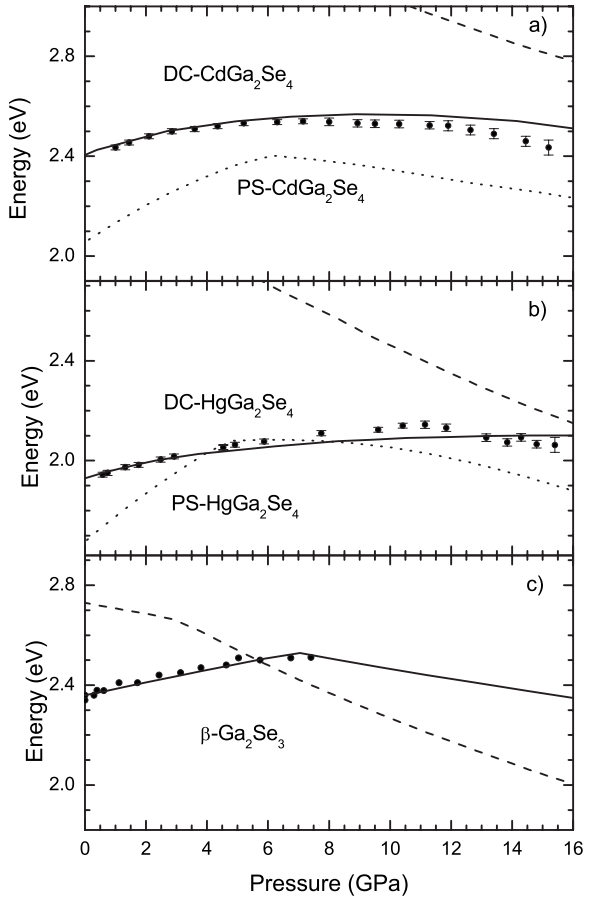

FIG. 4. (a) Pressure dependence of the band-gap energy in $CdGa_2Se_4$. Symbols correspond to experimental values for $I\bar{4}$ defect chalcopyrite (DC) phase. Theoretical calculations: direct band gap for DC phase (solid line), indirect Γ-Z band gap for DC phase (dashed line), direct band gap for $P\bar{4}2m$ pseudocubic (PS) phase (dotted line). (b) Same but for $HgGa_2Se_4$. (c) Pressure dependence of the band-gap energy in β-Ga_2Se_3. Symbols correspond to experimental data of the direct band gap taken from Ref. 7. Solid and dashed lines correspond to theoretical values of the direct and Γ-L indirect band gaps of the β phase. All calculated energies are upshifted to match the experimental direct band-gap energy at room pressure.

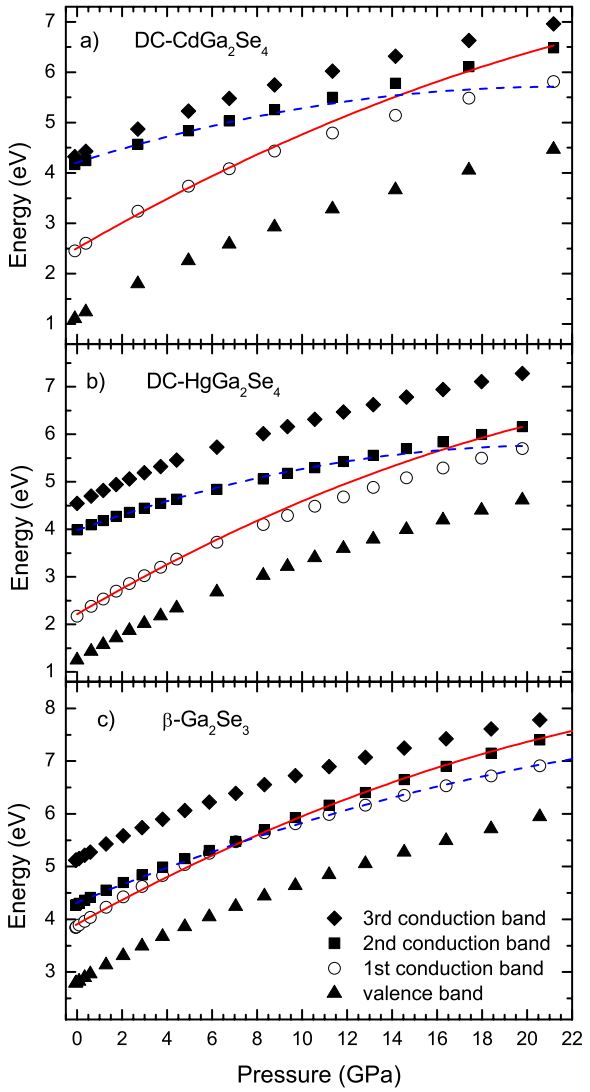

FIG. 5. (Color online) (a) Symbols: calculated pressure dependence of the energies of the topmost valence band and the lowest conduction bands at the Γ point for DC-$CdGa_2Se_4$. Solid (dashed) lines: expected pressure dependence of the first (second) conduction band energy in absence of band anticrossing. (b) Same for DC-$HgGa_2Se_4$. (c) Same for β-Ga_2Se_3.

salt structure. Our calculations in Fig. 4 (see dashed lines) indicate that the lowest indirect Γ-*Z* band gap in both compounds is higher in energy than the direct band gap at all pressures up to 16 GPa.

At room pressure, the direct band gap exhibits a pressure coefficient of 36 ± 4 meV/GPa (31 ± 3 meV/GPa) for DC-$CdGa_2Se_4$ (DC-$HgGa_2Se_4$) in very good agreement with our calculations. These values are rather small and similar to those of DC-$MnGa_2Se_4$ (25 meV/GPa[6]), monoclinic β-Ga_2Se_3 (45 meV/GPa[7]), and zincblende CdSe (37 meV/GPa[18]). The similar pressure coefficient of the four OVCs (DC-$CdGa_2Se_4$, DC-$HgGa_2Se_4$, DC-$MnGa_2Se_4$, and β-Ga_2Se_3) suggest that all AB_2X_4 and B_2X_3 adamantine OVCs with similar cation B and anion *X* share common features in their electronic band structures. Therefore, we have calculated the pressure dependence of the direct band gap in monoclinic β-Ga_2Se_3 in order to compare the electronic structure of binary and ternary OVCs. Figure 4(c) shows the experimental[7] and calculated pressure dependence of the direct band gap in β-Ga_2Se_3. A good agreement is observed between experimental and theoretical data for the direct band gap in this compound.

In order to understand the small pressure coefficients of the direct band gap in adamantine OVCs, Fig. 5 shows the calculated pressure dependence of the topmost VB and of the three lowermost CBs at Γ in DC-$CdGa_2Se_4$, DC-$HgGa_2Se_4$ and β-Ga_2Se_3. A very large calculated pressure coefficient of the topmost VB and lowermost CB energies, dE/dP, at room pressure is observed for the three compounds. With dE/dP values taken from Fig. 5, we can obtain the absolute band deformation potentials, $dE/d \ln V = B_0 \cdot dE/dP$, where V is the volume and B_0 is the bulk modulus. For DC-$CdGa_2Se_4$ [B_0=41.5 GPa (Ref. 10)], we obtain −10.2 eV and

−11.6 eV for the absolute deformation potentials of the topmost VB and lowermost CB at room pressure, respectively. For DC-$HgGa_2Se_4$ values of −10.6 eV and −11.8 eV are obtained for the VB and CB respectively by assuming a similar bulk modulus than for $CdGa_2Se_4$. Finally, for β-Ga_2Se_3 [B_0=51 GPa (Ref. 14)], we obtain absolute deformation potentials of −12.6 and −13.9 eV for the VB and CB. Notably, these values are more than a factor 3 higher than the highest absolute deformation potentials found in tetrahedrally coordinated binary compounds.[19] These large deformation potentials evidence a strong *d* cation character (more than 20%) of the topmost VB resulting in a strong *p*-*d* repulsion between several VBs. However, this fact does not explain why the absolute deformation potential of the VB in OVCs is much higher than in CdSe.[19] The reason for the high-deformation potential of the VB in OVCs is due to an additional increase of the pressure coefficient of the VB coming from the strong compressibility of the vacancy-anion distance. It can be observed in Fig. 1 that in OVCs anions have a lone electron pair because of the vacancy neighbor. Consequently, the topmost VB is composed of the higher-energy nonbonding anion orbitals corresponding to the lone electron pairs associated to the vacancies in OVCs. The presence of a lone electron pair in each anion results in a strong compressibility of the vacancy-anion distance that leads to a strong repulsion of nonbonding anion orbitals and consequently to a strong increase of the topmost VB energy with increasing pressure. This is the main reason for the strong increase in the topmost VB energy of OVCs on compression.

An even more striking feature of the direct band gap in DC-$CdGa_2Se_4$, DC-$HgGa_2Se_4$, DC-$MnGa_2Se_4$,[6] and β-Ga_2Se_3 is its strong nonlinear pressure dependence. Despite the different composition and crystalline structure of the above four compounds, the pressure coefficient is positive at room pressure, saturates at intermediate pressures, and even becomes negative in some of them at higher pressures. We have performed calculations in hypothetical PS-$CdGa_2Se_4$ and PS-$HgGa_2Se_4$ structures [see dotted lines in Figs. 4(a) and 4(b)] and they also show a strong nonlinear pressure dependence of the direct band gap. Thus suggesting a general nonlinear behavior of the direct band gap for all adamantine OVCs. Note that calculations for compounds with the DS structure are not easy to perform, because the disorder of cations in 2c and 2d positions cannot be simulated in a single unit cell. However, we expect a similar behavior of the electronic band structure in both DS and DC phases, as we will comment later. Therefore, we have reasons to claim that the nonlinear pressure dependence of the direct band-gap energy is a general characteristic of adamantine OVCs with $B_2^{III}X_3^{VI}$ and $A^{II}B_2^{III}X_4^{VI}$ stoichiometry, irrespective of their composition and structure. In the following we will give a justification for this general characteristic of OVCs.

Our calculations for DC-$CdGa_2Se_4$, for DC-$HgGa_2Se_4$, and for β-Ga_2Se_3 show that the strong nonlinear pressure dependence of the direct band gap is caused by: (i) a very strong positive pressure coefficient of the topmost VB, and (ii) a decrease in the positive pressure coefficient of the first CB on increasing pressure caused by a change of the cationic character of the first CB on increasing pressure. The latter is due to the change of the cationic character of the first CB on increasing pressure caused by the band anticrossing (BAC) of the two first CBs at Γ at high pressures. The BAC is evident in Fig. 5(a) for DC-$CdGa_2Se_4$ upon the comparison of the calculated pressure dependence of the first and second CBs with the expected behavior of both CBs in absence of BAC. Similar BACs of CBs are observed for DC-$HgGa_2Se_4$ and β-Ga_2Se_3 in Figs. 5(b) and 5(c), respectively. Unlike in ternary II-VI and III-V alloys, where the first CB suffers a BAC with a narrow band at higher energy than the first CB,[20,21] the BAC in tetrahedrally coordinated adamantine OVCs is between extended CBs, as it happens for octahedrally coordinated rocksalt-type lead chalcogenides.[22]

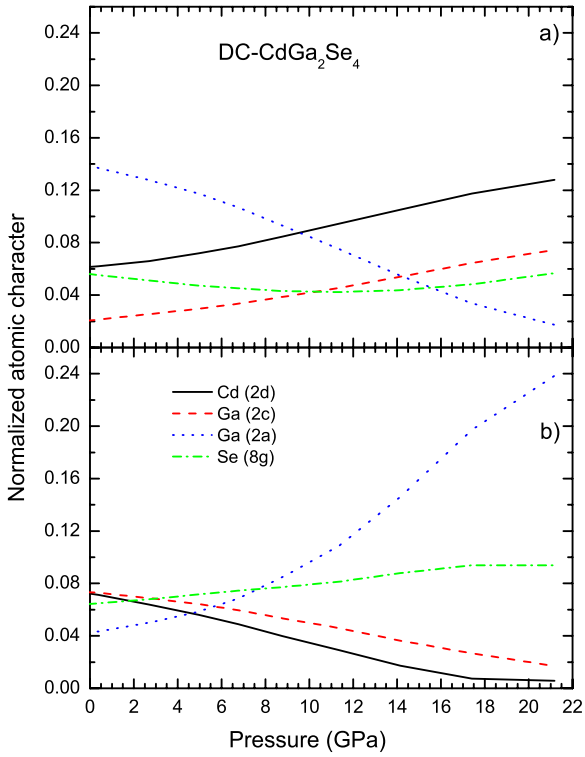

FIG. 6. (Color online) Atomic character of the first (b) and second (a) conduction band at the Γ point as a function of pressure for DC-$CdGa_2Se_4$. Wyckoff positions of the different atoms according to Fig. 1(a) are noted in parenthesis.

The calculated change of the cationic character of the first CB at high pressures caused by the BAC can be seen in Fig. 6 for DC-$CdGa_2Se_4$. In this figure, we show the pressure dependence of the normalized atomic character in the two lowermost CBs at Γ. Notations for the atomic characters refer to the different atoms located in their respective Wyckoff positions in the DC structure as shown in Fig. 1(a). At low pressures, the first CB is mainly contributed by the *s* character of Ga (2c) and Cd (2d) cations, the *p* character of Se, and a much smaller *s* character of Ga(2a). Contrarily, the second CB is mainly contributed by the *s* character of Ga (2a) with minor contributions of Se, Ga (2c) and Cd (2d). The BAC between the two lowermost CBs is evidenced by the opposite change of the cation character in both CBs on increasing pressure. A similar change of the atomic character of the first CB at Γ on increasing pressure is predicted theoretically to

occur in DC-$HgGa_2Se_4$ and β-Ga_2Se_3 (not shown) like that shown in Fig. 6 for DC-$CdGa_2Se_4$. In the following we will show that the cause of the BAC in OVCs is the presence of ordered vacancies in the unit cell.

Two are the main causes of the BAC in DC-$CdGa_2Se_4$ (and in other adamantine OVCs): (i) the equal symmetry of the first two CBs, which are close in energy and cannot cross each other on increasing pressure; and (ii) the larger pressure coefficient of the first CB than that of the second CB. It is the change of the cationic character of the first CB occurring in the BAC what causes the decrease of the pressure coefficient of the lowermost CB in OVCs and ultimately the strong decrease of the pressure coefficient of the direct band gap. Therefore, the question to answer is why the first CB has a larger pressure coefficient than the second CB at Γ in OVCs? In DC-$CdGa_2Se_4$, the different pressure coefficient of the two lowermost CBs is related to the existence of two non-equivalent Ga-Se bond distances, unlike in other tetrahedrally-coordinated binary and ternary compounds.[23] The existence of two non-equivalent Ga-Se bond distances is due to the presence of ordered vacancies. Figure 1(a) shows that Ga(2a) atoms and vacancies at 2b Wyckoff positions [also Ga (2c) and Cd (2d)] share the same crystallographic plane perpendicular to the *c* axis. On the basis of the calculations of Fig. 6, the large pressure coefficient of the first CB at room pressure is caused by its large Ga (2c) and Cd (2d) character and the large compressibility of the Cd (2d)-Se and Ga (2c)-Se bond distances.[10] On the other hand, the small pressure coefficient of the second CB at room pressure is caused by its large Ga (2a) character and the small compressibility of the Ga (2a)-Se bond distances.[10] The smaller compression of the Ga (2a)-Se bond distance is related to the high compressibility of the vacancies and the consequent elongation of the cation-anion bond distance in those cations sharing plane with vacancies; i.e., Ga (2a) in DC-$CdGa_2Se_4$.[2,10] Therefore, the opposite change of the cationic character between the first and second CBs in DC-$CdGa_2Se_4$ on increasing pressure leads to a reversal of their pressure coefficients at high pressure with respect to room pressure [see Fig. 5(a)]. The above explanation of the different pressure coefficients of the first and second CBs in DC-$CdGa_2Se_4$ is supported by the increase of the Ga (2c) and Cd (2d) contributions to the second CB and their decrease in the first CB on increasing pressure. This behavior is reasonable because the strong compression of the Ga (2c)-Se and Cd (2d)-Se distances as compared to that of Ga (2a)-Se one leads to an increase of the bonding-nonbonding energy difference that pushes upwards in energy the *s* orbitals of Ga (2c) and Cd (2d), being those of Ga (2a) less modified by pressure.

The strong nonlinear behavior of the direct band gap in DC-$HgGa_2Se_4$ and β-Ga_2Se_3 can be explained in a similar way than in DC-$CdGa_2Se_4$ by the BAC of the two first CBs [see Figs. 5(b) and 5(c)] due to the existence of several non-equivalent Ga-Se bond distances. The explanation given in the preceding paragraph allows us to predict a strong nonlinear pressure dependence of the direct band gap in other OVCs, like those with the DS structure (e.g., DS-$ZnGa_2Se_4$), because the disorder of cations at 2c and 2d positions is not expected to alter the cation contributions to the different CBs since cations in these two Wyckoff positions share the same crystallographic plane and are expected to contribute roughly in the same proportion to the first and second CBs (see Fig. 6).

V. CONCLUSIONS

We have evidenced a strong nonlinear pressure dependence of the direct band-gap energy in DC-$CdGa_2Se_4$, DC-$HgGa_2Se_4$, and β-Ga_2Se_3. Our calculations in several ordered-vacancy compounds reveal that the existence of ordered vacancies alter the cation-anion bond distances and their compressibilities resulting in the presence of non-equivalent cations with different contribution to different CBs at each pressure. At high pressures all OVCs seem to exhibit a band anticrossing between several CBs at Γ. The BAC results in a change of the cation character of the first CB that leads to a strong decrease in its pressure coefficient and consequently to a strong nonlinear pressure dependence of the direct band-gap energy. In summary, we propose that the strong nonlinear behavior of the direct band gap is characteristic to all adamantine $B_2^{III}X_3^{VI}$ and $A^{II}B_2^{III}X_4^{VI}$ OVCs, irrespective of their particular composition and structure.

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