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High-pressure optical and vibrational properties of $CdGa_2Se_4$: Order-disorder processes in adamantine compounds

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High-pressure optical absorption and Raman scattering measurements have been performed in defect chalcopyrite (DC) $CdGa_2Se_4$ up to 22 GPa during two pressure cycles to investigate the pressure-induced order-disorder phase transitions taking place in this ordered-vacancy compound. Our measurements reveal that on decreasing pressure from 22 GPa, the sample does not revert to the initial phase but likely to a disordered zinc blende (DZ) structure the direct bandgap and Raman-active modes of which have been measured during a second upstroke. Our measurements have been complemented with electronic structure and lattice dynamical *ab initio* calculations. Lattice dynamical calculations have helped us to discuss and assign the symmetries of the Raman modes of the DC phase. Additionally, our electronic band structure calculations have helped us in discussing the order-disorder effects taking place above 6–8 GPa during the first upstroke. © *2012 American Institute of Physics*. [doi:10.1063/1.3675162]

I. INTRODUCTION

Adamantine ordered-vacancy compounds (OVCs) constitute a class of compounds derived from the diamond or zinc blende structure with a different number of anions and cations and in which a cation site is vacant in an ordered and stoichiometric fashion. They are tetrahedrally coordinated compounds and include binary B_2X_3 compounds, like sesquisulfides and sesquiselenides, and ternary AB_2X_4 compounds. These latter compounds typically crystallize in one of three tetragonal structures: (i) the defect chalcopyrite (DC) structure with space group (S.G.) I-4, No. 82 [see Fig. 1(a)], (ii) the defect stannite (DS) structure with S.G. I-42 m, No. 121 [also known as defect famatinite, see Fig. 1(b)], and (iii) the pseudocubic (PS) structure (S.G. P-42 m, No. 111).

Despite their different structures, adamantine ternary compounds have in common, unlike in the zinc blende structure, the presence of several nonequivalent tetrahedrally coordinated cations. Consequently, the doubling of the cubic zinc blende unit cell along the *c* axis in these compounds results in a tetragonal symmetry that provides them with special properties not present in cubic zinc blende-type compounds. In particular, adamantine OVCs have important applications in optoelectronics, solar cells, and non-linear optics that have attracted considerable attention in the last 30 years as evidenced in several reviews.[1–4] In this sense, cadmium digallium selenide ($CdGa_2Se_4$) has considerable interest for optoelectronic applications. These semiconductors have potential applications in the field of non-linear optics,[2] photovoltaics,[5] and in diluted magnetic semiconductors.[6] OVCs are used as gyrotropic media in narrow-band optical filters, and in particular $CdGa_2Se_4$ has already found practical applications as a tunable filter and ultraviolet photodetector.[7,8] In addition, this compound is a promising optoelectronic material due to its high values of nonlinear susceptibility, optical activity, intense luminescence, and high photosensitivity.[2]

$CdGa_2Se_4$ is an OVC of the $A^{II}B_2^{III}X_4^{VI}$ family that crystallizes in the tetragonal DC structure[9,10] as depicted in Fig. 1(a), where Ga atoms occupy *2a* and *2c* sites, Cd atoms occupy *2d* sites, vacancies occupy *2b* sites, and Se atoms occupy *8g* sites. $CdGa_2Se_4$ is one of the most studied adamantine ternary compounds, and the behavior of DC-$CdGa_2Se_4$ under pressure has been subject of recent studies.[11–16] In particular, two Raman scattering measurements under pressure[11,12] found a phase transition near 20 GPa to the disordered rock salt (DR) structure [see Fig. 1(c)]. These two studies provided two different symmetry assignments of the Raman-active modes of the DC phase that were not discussed in the latter study despite their use of a Keating-Harrison model.[12] However, both studies agreed on the existence of two stages of cation disorder prior to the phase transition to

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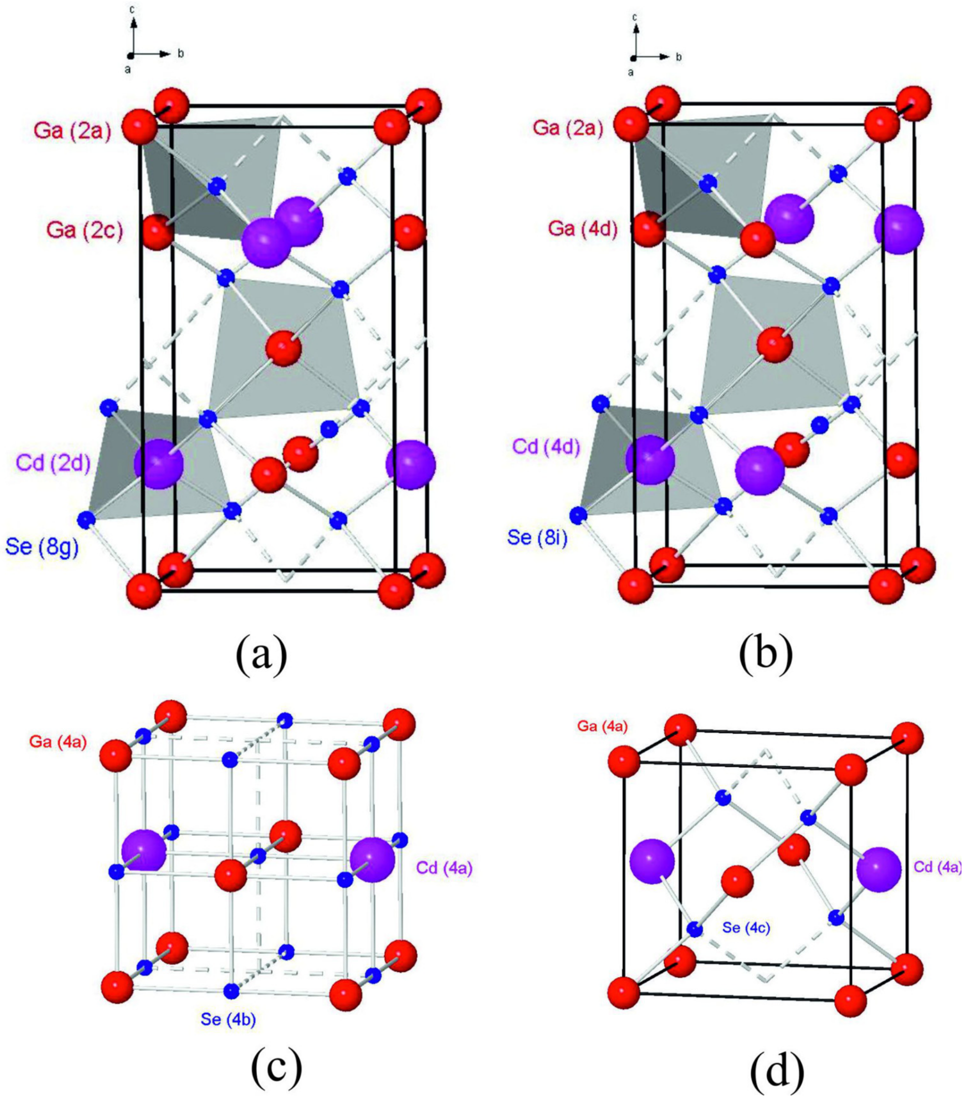

FIG. 1. (Color online) (a) Structure of the defect chalcopyrite (DC) $CdGa_2Se_4$, (b) defect stannite (DS) $CdGa_2Se_4$ (model 2 of Table II), (c) defect rock salt (DR) $CdGa_2Se_4$, and (d) defect zinc blende (DZ) $CdGa_2Se_4$. Big light atoms are Cd, medium dark atoms are Ga, and small dark atoms are Se. To distinguish between nonequivalent atoms in the DC and DS structures, the Wyckoff sites are given in parenthesis.

the DR phase on increasing pressure. The first stage consists of an initial cation disorder resulting in a phase transition from the DC to the DS structure, while the second stage involves total cation and vacancy disorder leading to the cubic disordered zinc blende (DZ) structure [see Fig. 1(d)]. In these two Raman works, the two stages of disorder were only discussed on the basis of the pressure dependence of the full width at half maximum (FWHM) of several Raman modes assuming that the two stages of disorder should occur in OVCs at high pressures in the same way that they were theoretically predicted for OVCs at high temperatures.[3] However, the evident changes in the Raman spectrum expected from these two order-disorder phase transitions and suggested by Eifler *et al.*[17,18] were not addressed in Refs. 11 and 12. In fact, the presence of two stages of cation disorder in OVCs was questioned by posterior *ab initio* lattice dynamics calculations in $CdGa_2Se_4$ and other OVCs.[13,14]

Recent x-ray diffraction (XRD) measurements up to 30 GPa in $CdGa_2Se_4$ confirmed a phase transition from the DC structure to the DR phase above 21 GPa.[15] This phase transition was found to be non-reversible, and on decreasing pressure, $CdGa_2Se_4$ was found to transform to a different metastable phase. The authors proposed that the observed XRD peaks of the new metastable phase could be explained by a cubic DZ structure, where one out of four cation sites is randomly occupied by a vacancy. This result is in contradiction with those of Refs. 11 and 12 since in these two works authors reported that the recovered sample at ambient pressure remained opaque because the phase transition to the DR phase was irreversible. As regards high-pressure studies in $CdGa_2Se_4$, recent optical absorption measurements in DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$ were conducted and provided evidence that all OVCs are expected to have a strong nonlinear pressure dependence of the direct bandgap energy at low pressures.[16]

In summary, previous high-pressure Raman scattering studies in DC-$CdGa_2Se_4$ were far from being conclusive because (i) there is some controversy regarding the assignment of the symmetries of the Raman-active modes, (ii) there is controversy regarding the presence of the two stages of disorder in this compound at high pressure; and (iii) there is controversy regarding the reversibility of the order-disorder phase transition leading from the DC to the DR structure taking place near 20 GPa in $CdGa_2Se_4$. Furthermore, the mechanisms of the order-disorder phase transitions are far from being completely understood[11,19–21] because these stages of disorder are difficult to be evidenced by x-ray diffraction measurements. Therefore, in this work, we report high-pressure optical absorption and Raman scattering measurements at room temperature in DC-$CdGa_2Se_4$ during two upstrokes above 22 GPa and two downstrokes. Our measurements are complemented with theoretical *ab initio* calculations of the electronic structure and lattice dynamics in DC-$CdGa_2Se_4$ till 20 GPa. The aim of this work is to help in the correct assignment of the symmetry of the Raman active modes of the DC phase, to show that the DC to DR phase transition do not occur as a consequence of two stages of disorder, and to shed light into the complex pressure-induced order-disorder transitions taking place in $A^{II}B_2^{III}X_4^{VI}$ OVCs. In particular, we will show that in DC-$CdGa_2Se_4$ under certain circumstances the DC-to-DR phase transition is irreversible and that a new phase, likely being the DZ phase, can be recovered on downstroke. The paper is organized as follows: Secs. II and III are devoted to the experimental and theoretical details and Sec. IV is devoted to present the results and discussion of both the optical absorption and Raman scattering measurements with the help of our theoretical calculations. Finally, the main conclusions are presented in Sec. V.

II. EXPERIMENTAL DETAILS

Single crystals of DC-$CdGa_2Se_4$ are grown from its constituents CdSe and Ga_2Se_3 by chemical vapor transport method using iodine as a transport agent.[22] The as-grown crystals represent triangular prisms with mirror surfaces. Chemical and structural analyses have shown the stoichiometric composition of the crystals with no spurious phases. The samples used in the optical absorption measurements had almost parallel faces with around 20 μm in thickness and 100×100 μm^2 in size. The samples were loaded together with a 16:3:1 methanol-ethanol-water mixture in the 250 μm diameter hole of an Inconel gasket inside a membrane diamond anvil cell. Ruby grains were used for pressure calibration.[23] High-pressure absorption experiments at room temperature were performed by the sample-in sample-out method using a micro-optical system[24] in combination with a tungsten lamp and an Ocean Optics spectrometer. High-pressure Raman scattering measurements at room temperature were performed with a LabRAM HR UV microspectrometer coupled to a Peltier-cooled CCD camera and using a 632.81 nm (1.96 eV) HeNe laser excitation line with a power of 10 mW and a spectral resolution better than 2 cm^{-1}. To analyze the Raman spectra under pressure, Raman peaks have been fitted when possible to a Voigt profile (Lorentzian profile convoluted by a Gaussian due to the limited resolution of the spectrometer) where the spectrometer resolution is a fixed parameter.

III. *AB INITIO* CALCULATIONS

Details of the *ab initio* total energy and electronic structure calculations in DC-$CdGa_2Se_4$ within the framework of the pseudopotential method and the density functional theory with the Vienna Ab initio Simulation Package (VASP) code and using the generalized gradient approximation can be consulted in Ref. 16. Lattice dynamics calculations of phonon modes were performed in the defect chalcopyrite structure at the zone center (Γ point) of the Brillouin zone. For the calculation of the dynamical matrix at the Γ point, we used a direct force-constant approach (or supercell method)[25] that involves separate calculation of the forces in which a fixed displacement from the equilibrium configuration of the atoms within the primitive unit cell is considered. The calculations provided information about the frequency, symmetry, and polarization vector of the vibrational modes. Highly converged results on forces are required for the calculation of dynamical matrix of lattice dynamics calculations. For that reason, we used a dense grid of k-special points for integrations along the Brillouin zone. At each selected volume, the structures were fully relaxed to their equilibrium configuration through the calculation of the forces on atoms and the stress tensor.[26] In the relaxed equilibrium configuration, the forces are less than 0.004 eV/Å, and the deviation of the stress tensor from a diagonal hydrostatic form is less than 1-2 kbar.

IV. RESULTS AND DISCUSSION

A. Raman scattering

1. *First upstroke*

Group theoretical considerations indicate that the I-4 structure of DC-$CdGa_2Se_4$ has 15 vibrational modes with the following representation $\Gamma = 3A(R) + 6B(R;IR) + 6E(R;IR)$. The A modes, here noted A^1 to A^3 as a function of increasing frequency, are non-polar Raman active modes while B and the doubly degenerated E modes, here noted from 1 to 5 on increasing frequency, are polar modes that are both Raman (R) and infrared (IR) active and therefore exhibit longitudinal-transversal optic (LO-TO) splitting. Two of the 15 vibrational modes (an E mode and a B mode) are acoustic modes. In this way, we expect 13 Raman-active optical modes: $3A + 5B + 5E$; however taking into account the LO-TO splittings, it should be possible to measure a maximum of 23 Raman-active first-order optical modes in Raman experiments.

Figure 2 shows the room-temperature Raman spectra of DC-$CdGa_2Se_4$ at different pressures up to 20 GPa. The Raman spectrum of DC-$CdGa_2Se_4$ can be divided into two regions, the low- and high-frequency regions below and above 150 cm^{-1}, respectively. The Raman modes at the low-frequency region involve mainly the group-II cation (Cd in our case), while the Raman modes at the high-frequency region involve mainly the group-III cation (Ga in our case).[27] This is especially true in DC-$CdGa_2Se_4$ because the Cd atom is considerably heavier than the Ga atom. In our experiments, we measured 15 Raman-active modes, including 3 non-polar A modes and 12 polar modes. The polar modes correspond mainly to TO modes plus three LO modes due to the TO-LO splitting of the E^3, E^5, and B^5 modes as will be discussed later. The most intense peak of the Raman spectrum corresponds to the lowest frequency A mode, named A^1. This mode is also known as the "breathing" mode because it is associated to the symmetric oscillation of the anions against the stoichiometric vacancy.[11] It must be noted

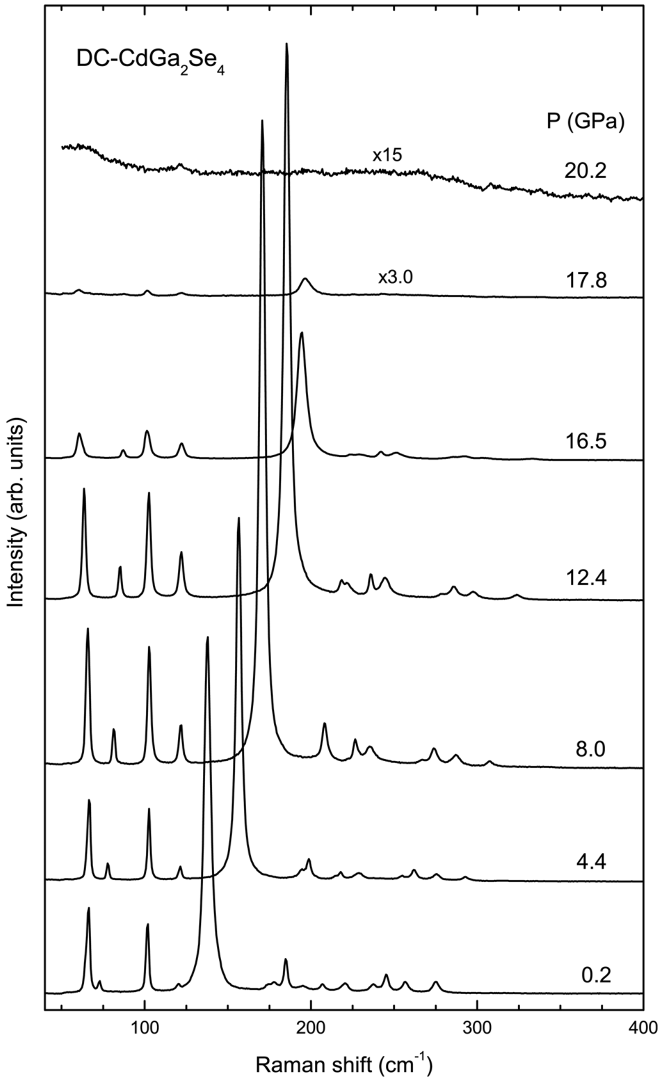

FIG. 2. Room-temperature Raman scattering spectra of DC-CdGa$_2$Se$_4$ up to 20.2 GPa.

that the non-polar A modes in OVCs correspond to oscillations of the anions around the vacancy so the frequencies of the A modes are barely affected by the cation masses and scale with the anion mass. On the other hand, the B modes correspond to vibrations of cations and anions in the z direction while the E modes correspond to vibrations of cations and anions in the x-y plane.[11]

As pressure increases, the Raman peaks of the high-frequency region shift to higher frequencies while most of the peaks of the low-frequency region show a negligible or even negative pressure coefficient. Above 18 GPa, all Raman peak intensities are hardly seen, thus indicating the onset of a phase transition that is completed at 20.2 GPa with the disappearance of all the Raman peaks of the DC phase. We have assigned the high-pressure phase of CdGa$_2$Se$_4$ to the Raman-inactive DR phase, in good agreement with XRD measurements.[15]

The evolution of the Raman peak frequencies (symbols) as a function of pressure for DC-CdGa$_2$Se$_4$ is shown in Fig. 3 and compared to our a*b initio* calculated frequencies (lines). Our calculations only provide the frequencies of the TO modes of both B and E polar modes. In general, a rather good agreement between experimental and theoretical frequencies and pressure coefficients can be observed. Therefore, we have used our *ab initio* calculations as a help to assign and discuss the symmetry of the measured Raman modes and their possible TO-LO splitting and to compare them with previous measurements and calculations.[11–13]

The zero-pressure frequencies, pressure coefficients, and derivatives of the pressure coefficients for experimental and calculated Raman modes in DC-CdGa$_2$Se$_4$ are summarized in Table I and compared with the experimental results of Ursaki *et al.*[11] In general, our assignment of the Raman mode frequencies agrees with those of Ursaki *et al.*[11] and also with those of Mitani *et al.*[12] The main difference between ours and previous results is the assignment of the last three high-frequency modes. Thanks to our lattice dynamical calculations and the comparison of the experimental and calculated frequencies and pressure coefficients, we tentatively assign the modes observed at 244, 257, and 274 cm^{-1} to the $E_{TO}{}^5$, $B_{TO}{}^5$, and $E_{LO}{}^5 + B_{LO}{}^5$ modes, respectively, while Ursaki *et al.* assigned the modes at 245, 258, and 275 cm^{-1} to the $E_{LO}{}^4$, $E_{TO}{}^5 + B_{TO}{}^5$, and $E_{LO}{}^5 + B_{LO}{}^5$ modes, respectively, which was based in a previous Raman work.[28] A rather different assignment was done by Mitani *et al.*, who assigned the

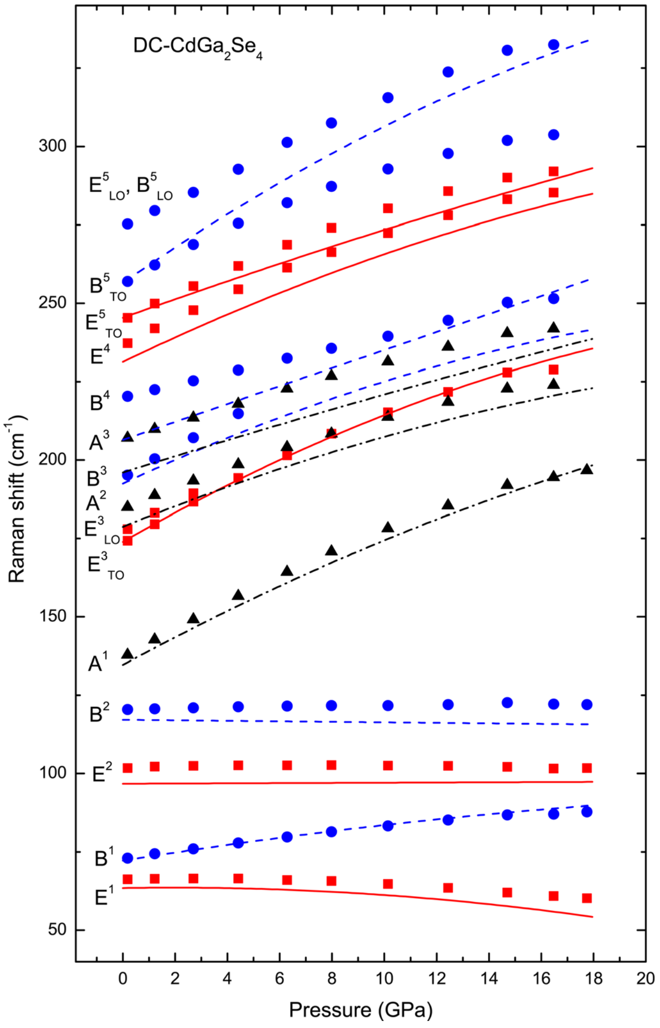

FIG. 3. (Color online) Pressure dependence of the experimental (symbols) and calculated (lines) vibrational modes in DC-CdGa$_2$Se$_4$.

TABLE I. Experimental and calculated Raman-mode frequencies at room pressure and their pressure coefficients in DC-$CdGa_2Se_4$ as obtained from fits to the data using equation, $\omega = \omega_0 + aP + bP^2$, where ω_0 is expressed in cm^{-1}, a in cm^{-1} GPa$^{-1,}$ and b in -100 cm^{-1} GPa^{-2}.

Mode (symmetry)	ω_0 (exp.)[a]	a (exp.)[a]	b (exp.)[a]	ω_0 (th.)[b]	a (th.)[b]	b (th.)[b]	ω_0 (exp.)[c]	a (exp.)[c]	b (exp.)[c]
E^1	66	0.11	2.67	63.5	0.14	3.64	66	0.30	3.66
B^1	73	1.30	2.52	72.2	1.34	1.97	73	1.28	2.21
E^2	102	0.20	1.22	96.7	0.03		102	0.24	1.32
B^2	120	0.22	0.65	117.2	-0.08		121	0.28	0.95
A^1	137	5.05	9.15	134.7	4.51	5.39	138	4.85	7.23
${E_{TO}}^3$	173	5.31	11.35	173.9	4.81	7.68	176	5.73	14.56
${E_{LO}}^3$	177	4.52	7.89						
A^2	184	3.63	7.13	178.7	3.38	5.08	185	3.56	6.45
B^3	194	5.10	10.16	192.5	3.91	6.55	194	4.81	
A^3	206	2.92	4.33	196	2.64	1.48	207	2.74	2.71
${B_{TO}}^4$	220	1.98	0.08	206.4	2.87		221	2.43	2.76
${B_{LO}}^4$							226	3.12	6.17
${E_{TO}}^4$	237	4.49	9.18	231.3	4.00	5.65	238	4.41	8.50
${E_{LO}}^4$							245	4.45	8.78
${E_{TO}}^5$	244	4.49	9.51	245.4	2.99	1.87	258[d]	5.44[d]	13.77[d]
${B_{TO}}^5$	257	4.80	11.72	256.5	5.84	8.38			
${(E+B)_{LO}}^5$	274	4.90	7.47				275	4.90	6.23

[a] Present measurements.
[b] Present *ab initio* calculations.
[c] Reference 11.
[d] Authors in Ref. 11 assign this Raman peak to symmetry ${E_{TO}}^5$, ${B_{TO}}^5$.

modes at 242, 255, and 272 cm^{-1} to the ${E_{LO}}^4$, ${E_{LO}}^5$, and ${B_{LO}}^4$ modes, respectively.[12] Therefore, we think that in contrast with previous measurements, we have not observed the ${E_{LO}}^4$ mode or this mode is coincident in frequency with one of the three modes of highest frequency. Finally, as regards to *ab initio* calculations, we have to mention that our calculated Raman frequencies, pressure coefficients, and ordering of the different modes are in rather good agreement with previous *ab initio* calculations of Fuentes-Cabrera.[13] Our calculated frequencies are slightly smaller than those of Fuentes-Cabrera because we have used the generalized gradient approximation (GGA) instead of local density approximation (LDA) for the exchange and correlation energy. The main difference between both calculations occurs for the E^2 and B^2 modes, the experimental pressure coefficients of which at ambient pressure are small but positive and have been calculated to be almost negligible for GGA calculations and slightly negative for LDA calculations.

From now on we are going to discuss the possible stages of pressure-induced disorder taking place at cation sites in DC-$CdGa_2Se_4$, prior to the pressure-induced DC-to-DR phase transition, on the basis of Raman scattering measurements. In previous high-pressure Raman works, the disorder process at cation sites in OVCs with DC or DS structure was mainly suggested on the light of the extraordinary changes of the intensity and width of some Raman modes above certain pressures.[11,12,19,20,29] Indeed, cation disorder should affect drastically the intensities and widths of Raman modes because it is known that cation disorder in the DS structure results in broader Raman spectra with overlapped and less intense peaks than Raman spectra of the DC phase.[30] Therefore, to discuss the possible disorder processes occurring in DC-$CdGa_2Se_4$ at cation sites, we have plotted the FWHM and the intensity of the most intense Raman modes in Figs. 4 and 5, respectively. Figure 4 shows that the FWHM for modes A^1, E^1, and B^1 decreases up to about 4 GPa, stays more or less constant up to 8-10 GPa, and increases above this pressure up to the phase transition to the DR structure. These results are in relatively good agreement with Fig. 5(b) of Ref. 11. On the other hand, Fig. 5 shows the absolute intensity of the A^1 mode, which is the most intense mode, and the relative intensities of other Raman modes normalized to that of the A^1 mode. This figure shows that the intensity of

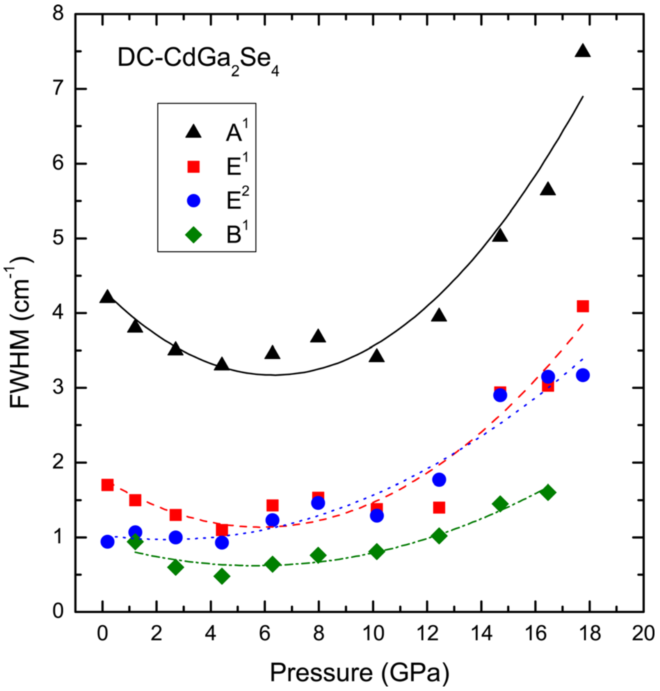

FIG. 4. (Color online) FWMH of the A^1, E^1, E^2, and B^1 Raman-active modes of DC-$CdGa_2Se_4$ during the first pressure cycle.

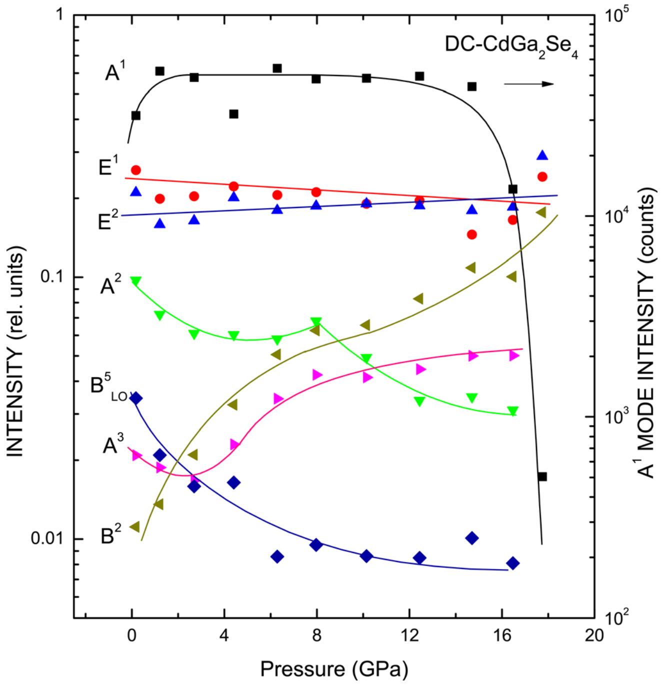

FIG. 5. (Color online) Right vertical axis: Intensity of the A^1 mode for DC-CdGa$_2$Se$_4$ as a function of pressure. Left vertical axis: Intensities of other modes for DC-CdGa$_2$Se$_4$ normalized to that of the A^1 mode as a function of pressure.

the A^1 mode (squares) remains almost constant up to 14 GPa and decreases above this pressure. A similar decrease of the intensity of the A^1 mode above 11 GPa was also observed in a previous work.[11] Furthermore, we have noted a decrease of the intensity of the A^2 mode (down triangles) above 8 GPa in good agreement with Ursaki's *et al.* results.[11]

In the following, we will analyze our Raman results to discuss the possible stages of pressure-induced disorder in DC-CdGa$_2$Se$_4$. To help to the discussion of the different stages of pressure-induced disorder in OVCs leading from the DC phase to the DZ phase (both tetrahedrally-coordinated structures), we have summarized in Table II the possible disordered structures which are intermediate between these two phases. Table II includes different tetragonal DS (S.G. I-42 m, No. 121) and disordered CuAu-like (DCA) phases (S.G. P-4m2, No. 115). As regards DS phases, it includes the structures proposed by Eifler *et al.* (first four models),[17,18] plus one additional DS structure (model 5) coming from the cation disorder at both *2b* and *4d* sites in models 1 and 4. Curiously, the DS phase of model 5, where B^{III} cations and vacancies mix at both *2b* and *4d* sites, seems to be the case of β-HgGa$_2$Te$_4$ where the c/a ratio is approximately 2.[10] Additionally, we include the possible DCA phases[31] obtained by assuming additional cation disorder between *2a* and *2b* sites in the different models of the DS structure and that have not been considered before. We must stress that models 6-10 come from models 1-5, respectively, because *2a* and *2b* sites become indistinguishable due to disorder and lead to a *1a* site in the DCA structure. Similarly, the *4d* site of the DS phase becomes a *1c* site in the DCA structure, and the anion *8i* site of the DS phase becomes a *2g* site in the DCA phase.[31] Note also that cations at *1a* and *1c* sites in the DCA structures are clearly different and that additional cation disorder in the *1a* and *1c* sites of the DCA phases leads to the DZ structure as a final stage of cation disorder. Now the question is whether DC-CdGa$_2$Se$_4$ undergoes a pressure-induced total cation disorder leading from the DC to the DZ structure prior to the pressure-induced phase transition to the totally disordered rock salt phase (DR) in OVCs. In the following, we will show that our Raman measurements support the presence of only one stage of disorder above 6–8 GPa, leading from the DC to the DS phase in CdGa$_2$Se$_4$, but not a second stage of disorder above 11 GPa going from the DS to the DZ phase prior to the transition to the DR phase near 20 GPa.

In our opinion, the increase of the FWHM of almost all Raman modes above 6-8 GPa in DC-CdGa$_2$Se$_4$ clearly indicates the onset of a first stage of cation disorder that is supported by the decrease of the intensity of the A^2 mode above 8 GPa in good agreement with Ursaki *et al.*[11] In fact, the gradual decrease of the intensity of the A^2 mode is consistent with the partial transformation from the DC to the DS structure on increasing pressure according to two possible DS structures. One structure would have a partial cation disorder at *2c* and *2d* sites resulting in a *4d* site of the DS phase (model 2 in Table II). The other structure would have a total cation disorder at *2a*, *2c*, and *2d* sites resulting in disorder at both *2a* and *4d* sites of the DS phase (model 3 in Table II). Note that 12 Raman-active modes are expected in these two (model 2 and 3) DS structures; i.e., one non-polar *A* mode less than in the DC phase. In this respect, we must stress that also 12 Raman-active modes are expected in model 1 of Table II, but this DS structure is highly improbable at high pressures in DC-CdGa$_2$Se$_4$ because there is no cation disorder in this DS structure, and it will require a total interchange

TABLE II. Types of cation and vacancy distribution within I-42m and P-4m2 phases, which are intermediate between defect chalcopyrite (I-4) and disordered zincblende (F-43m) structures.

			I-42m space group (DS structure)		
Wyckoff site	Model 1	Model 2	Model 3	Model 4	Model 5
2a (0,0,0)	2 A^{II}	2 B^{III}	2/3 (A^{II} + 2B^{III})	2 A^{II}	2 A^{II}
2b (0,0,1/2)	2 V	2 V	2V	2 B^{III}	2/3 (V + 2B^{III})
4d (0,1/2,1/4)	4 B^{III}	2 (A^{II} + B^{III})	4/3 (A^{II} + 2B^{III})	2(V + B^{III})	4/3 (V + 2B^{III})
			P-4m2 space group (layered CuAu-like structure)		
	Model 6	Model 7	Model 8	Model 9	Model 10
1a (0,0,0)	2 (V + A^{II})	2 (V + B^{III})	2/3 (A^{II} + 3V + 2B^{III})	2(A^{II} + B^{III})	2/3 (3A^{II} + V + 2B^{III})
1c (1/2,1/2,1/2)	4 B^{III}	2 (A^{II} + B^{III})	4/3 (A^{II} + 2B^{III})	2 (V + B^{III})	4/3 (V + 2B^{III})

of Ga atoms at *2a* sites and Cd atoms at *2d* sites in the initial DC structure of $CdGa_2Se_4$. Finally, a DS structure in $CdGa_2Se_4$ at high pressures like models 4 and 5 in Table II is also improbable because (i) all Cd atoms should occupy the *2a* site of Ga atoms, like in model 1 and (ii) they have at least partially occupied *2b* sites, and according to group theory, they would imply the appearance of two extra polar B and E modes in the Raman spectrum additionally to the disappearance of the A^2 mode of the DC phase. Since no new Raman modes have been observed at high pressures in DC-$CdGa_2Se_4$, these two DS structures can be discarded to occur at high pressures in our compound. Therefore, we can conclude that our Raman measurements can be interpreted on the basis of a partial transformation from the DC to the DS structure (models 2 or 3 in Table II) above 6-8 GPa in agreement with Ursaki *et al.*[11]

It is noteworthy that despite the fact that Raman measurements support the existence of cation disorder resulting in a partial transformation from the DC to the DS phase, XRD measurements up to 21 GPa do not show evidence of a change in diffraction peaks supporting this phase transition;[15] however, this is not surprising because on one hand, the transition is not completed, and XRD measurements have difficulty in detecting minor phases in a mixture of phases, and on the other hand, both structures have the same systematic absences in the indexed lattice planes so they are very difficult to distinguish, even as pure phases. However, a deeper analysis of XRD data can be done if we compare experimental and theoretical data. Figure 6 shows the experimental and theoretical pressure dependence of the unit-cell volume and *c*/*a* ratio in DC-$CdGa_2Se_4$. It is clear that the decrease of the experimental volume with increasing pressure[15] is considerably smaller than the one expected from our theoretical calculations, which do not include any kind of disorder. On the other hand, there is an increase of the experimental *c*/*a* ratio with increasing pressure[15] which is much smaller than the increase of the *c*/*a* ratio theoretically predicted. It is known that the *c*/*a* ratio at ambient pressure is much smaller for DC than for DS compounds and that the cation disorder is favored on decreasing the tetragonal distortion; i.e., when *c*/*a* tend to 2.[10,32] In fact, the *c*/*a* ratio of DC structures with Ga and Se, like $CdGa_2Se_4$ and $HgGa_2Se_4$, is close to 1.90 while that of the DS structure of $ZnGa_2Se_4$ is around 1.98.[21] Therefore, the increase of the c/a ratio with pressure cannot be attributed to the increase of cation disorder on increasing pressure in DC-$CdGa_2Se_4$. However, the much smaller increase of the experimental c/a ratio with pressure than the theoretical one above 6 GPa suggests a partial transformation from the DC to the DS structure above this pressure in good agreeement with our Raman results and with the optical absorption measurements discussed in the next section. Assuming a similar decrease of the *a* lattice parameter under pressure in the DC and DS phases, the increase of the *c*/*a* ratio under pressure would result in an elongation of the atomic bonds along the *c* axis of the tetragonal structure, resulting in an small increase of the unit-cell volume of the DS phase with respect to the DC phase. Assuming a mixture of DC and DS phases at high pressures, this fact could explain the smaller decrease of the experimental volume with pressure with respect to theoretical values that assume no cation disorder. Therefore, our analysis indicates that both Raman and XRD measurement show a clear pressure-induced order-disorder phase transition leading from the DC to the DS structure in $CdGa_2Se_4$.

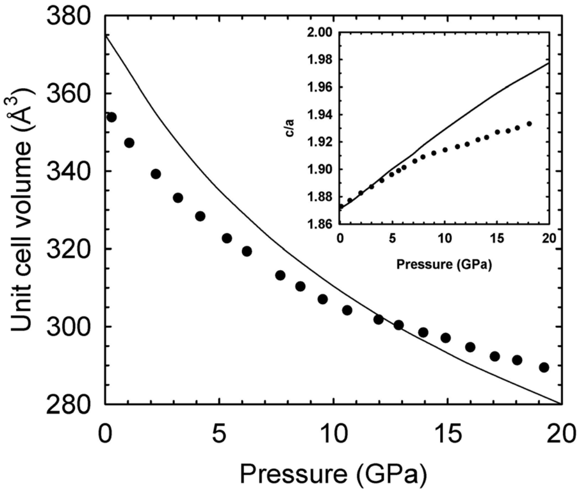

FIG. 6. Experimental (symbols) and theoretical (line) pressure dependence of the unit-cell volume and *c*/*a* ratio (inset) in DC-$CdGa_2Se_4$ up to 20 GPa. Experimental data are taken from Ref. 15.

As a final comment regarding the first stage of disorder, we have to note that Ursaki *et al.* used the decrease of the E^1 mode frequency above 8 GPa to support the existence of the first stage of cation disorder leading from the DC to the DS phase.[11] In this sense, Fuentes-Cabrera *et al.*[13,14] questioned the presence of any kind of disorder because the decrease in frequency with increasing pressure was already explained by calculations in DC-$CdGa_2Se_4$ without considering disorder. Our calculations also yield a negative pressure coefficient for the E^1 mode above 4 GPa in agreement with ours and previous Raman measurements and with calculations of Fuentes-Cabrera *et al.* Therefore, we think that the argument related to the E^1 mode used by Ursaki *et al.* is not consistent to support the first stage of cation disorder. This leads to the question regarding the convenience of using Raman mode frequency changes in the discussion of order-disorder phase transitions.

As regards the effect of disorder on the Raman mode frequencies, one would expect *a priori* that cation disorder leading from the DC to the DS phase should not affect the pressure dependence of the Raman mode frequencies because many frequencies depend on the reduced mass and bonding force between the atoms, and these parameters are similar in both DC and DS structures. However, taking into account the increase of the experimental *c*/*a* ratio with increasing pressure experimentally found in DC-$CdGa_2Se_4$[15] and assuming a similar decrease of the *a* lattice parameter under pressure in the DC and DS phases, the increase of the *c*/*a* ratio under pressure would result in an increase of the unit-cell volume, as already commented, and in an elongation of the atomic bonds along the *c* axis of the tetragonal structure resulting in a decrease of the pressure coefficient of the *B* modes with increasing pressure. In this sense, the less positive pressure coefficient that we have measured for the experimental B^4 and B^5 modes than those obtained by theoretical calculations (see Fig. 3) could be interpreted as the result of the continuous cation disorder process leading from the DC to the DS phase.

Let us now discuss the possible second stages of pressure-induced disorder in DC-$CdGa_2Se_4$ on the light of Raman data. In OVCs, a series of phase transformations from the ordered DC phase to the completely disordered DZ phase would likely go through the intermediate DS and DCA structures shown in Table II. Therefore, after the DS phase, one would think in a possible pressure-induced phase transition to a DCA phase. These layered structures are considerably more symmetric than the DC and DS phases and have only six Raman-active modes (A_1+2B_2+3E) with the A mode being the non-polar mode and the B_2 and E being polar modes showing TO-LO splitting. Therefore, one A mode is lost at the DS-to-DCA phase transition. In this respect, our Raman measurements at pressures above 11 GPa clearly show more than six Raman modes and the presence of both the A^1 and A^3 modes with some remnant A^2 mode, corresponding to the DC phase up to 18 GPa. Above this pressure all Raman modes decrease in intensity showing evidence of a phase transition to the Raman-inactive DR phase. Therefore there is no indication showing a second stage of cation disorder in DC-$CdGa_2Se_4$ prior to the pressure-induced phase transition to the DR phase going through the DCA phase.

Let us now discuss the final stage of cation and vacancy disorder, i.e., the transition from the DS directly to the DZ phase. The zinc blende structure is much more symmetric than the DC and DS phases and only has one polar Raman-active mode showing TO-LO splitting. However, the Raman spectrum of the DZ phase would rather resemble that of the first-order one-phonon density of states of the zinc blende phase because disorder of cations and vacancies at cation sites will promote defect-induced or defect-assisted Raman scattering (DARS) due to the loss of the translational symmetry of the crystal. This Raman activity has been observed in many disordered, nanocrystalline, and pressure-treated compounds;[33–36] however, as already commented, no Raman scattering similar to a one-phonon density of states of the zinc blende phase has been ever reported to occur at high pressures neither above the pressure range 11-14 GPa in DC-$CdGa_2Se_4$ nor in other adamantine ternary OVCs at high pressures.[11,12,19,20] In fact, Ursaki *et al.* concluded, from the analysis of their Raman results,[11] that the decrease of the intensity of the A^1 mode above 11 GPa was due to the onset of a second stage of disorder where all cations and vacancies mixed together, thus leading to the DZ phase in good agreement with the theoretically predicted stages of disorder proposed by Bernard and Zunger for OVCs at high temperatures but not for high pressures.[3] The same argument has been used in posterior studies of OVCs under high pressure.[12,20] We believe that the decrease of the intensity of the A^1 mode was misinterpreted by Ursaki *et al.* and other authors as a signal of the onset of the formation of a DZ phase in OVCs at high pressures.[11,19] Instead, we attribute the decrease of the intensity of all the modes above 14 GPa, specially measured for the A^1 mode (the last one to be observed prior to the phase transition), to the local nucleation of the high-pressure DR phase; which is evidenced as dark linear defects in the sample above that pressure. These dark linear defects, which are precursors of the pressure-induced phase transition from tetrahedrally coordinated semiconductor phases toward octahedrally coordinated metallic phases, have been observed in many semiconductors and cause considerable optical scattering leading to band tailing as will be discussed in the next section. In fact, dark linear defects precluding Raman and optical absorption measurements can be observed in InSe up to 3 GPa prior to the complete semiconductor-to-metal transformation,[37] and it is expected that this pressure can be even larger in defective compounds like OVCs. We think that the mistake in the interpretation of the decrease of the A^1 intensity as the onset of the second stage of disorder was motivated by the belief that two stages of cation disorder should occur at high pressures in analogy with the two stages of cation disorder that were theoretically predicted to occur at high temperatures.[3] However, we have to note that on increasing temperature atomic vibrations increase in amplitude and disorder is promoted so the two stages of disorder that lead from the DC phase to the DZ phase are reasonable. This is not the case on increasing pressure, where atomic vibrations are hindered. Consequently, the phase transition from the DC or DS phases to the DZ structure is not expected to occur at high pressures. Further support to the absence of DCA and DZ phases at high pressures as a second stage of pressure-induced disorder are given in the next paragraphs and sections.

The last objective of this section is to discuss the reversibility of the DC-to-DR phase transition in DC-$CdGa_2Se_4$. To that purpose, we have performed Raman measurements during downstroke slowly decreasing pressure down to 1.0 GPa after transiting the DC-$CdGa_2Se_4$ sample to the DR phase at 20 GPa. We show in Fig. 7 the comparison of the Raman spectra obtained at similar pressures for DC-$CdGa_2Se_4$ on upstroke and downstroke. The Raman spectrum on downstroke at 1.0 GPa differs considerably from the Raman spectrum on upstroke at 1.2 GPa. The Raman spectrum on downstroke shows very broad, and in some cases asymmetric, peaks in contrast to the narrow peaks during upstroke at a similar pressure. The broad Raman spectrum of

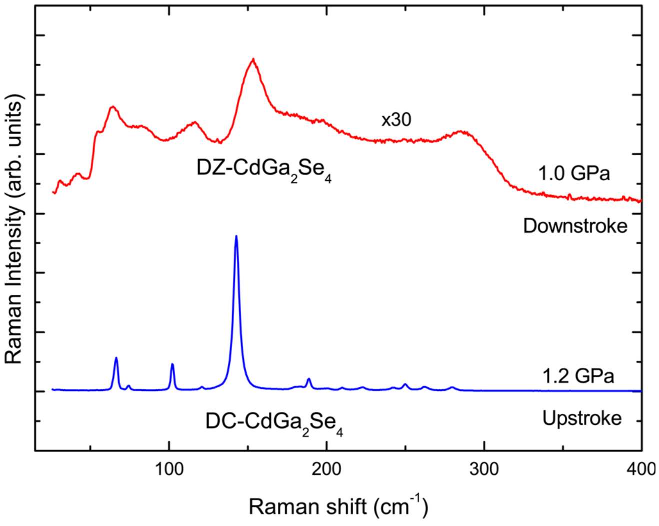

FIG. 7. (Color online) Raman spectra of the $CdGa_2Se_4$ in the first upstroke at 1.2 GPa and in the first downstroke at 1.0 GPa with defect chalcopyrite and disordered zinc blende phase, respectively.

the recovered phase looks like a one-phonon density of states of the zinc blende phase and in particular of zinc blende-type ZnSe.[38] Note that the Raman mode frequencies on downstroke correlate well with those of the DC phase on upstroke. In particular, it must be noted that the most intense Raman mode of the recovered sample is close in frequency to the dominant mode of the DC phase, i.e., the breathing mode. Clearly, our Raman spectrum on downstroke cannot be attributed to the DR phase, which is Raman inactive, but also it does not correspond to the initial DC phase. Because the DR phase is a totally disordered phase, we have attributed the Raman spectrum on downstroke at 1.0 GPa to the totally disordered zinc blende phase (DZ). This result is in agreement with the results of Grezchnik *et al*.[15] and contrasts with the non observation of Raman signal on downstroke in previous high-pressure Raman measurements in $CdGa_2Se_4$.[11,19] We have to note that the DZ phase has been also recently found by XRD measurements in other OVCs on decreasing pressure from the DR phase.[39] This different behavior in $CdGa_2Se_4$ can be justified by the speed of pressure decrease because a quick decrease of pressure can lead to quenching of the high-pressure DR phase at ambient pressure as observed in Refs. 11 and 12.

In summary, we conclude that high-pressure XRD and Raman measurements support the existence of only one stage of cation disorder resulting in a partial transformation from the DC to the DS phase above 6-8 GPa prior to the pressure-induced transition to the DR structure. No second phase of disorder seems to take place in DC-$CdGa_2Se_4$ above 11-14 GPa, and the decrease of the intensity of all modes above this pressure is likely due to the partial transformation of the sample to the DR phase above this pressure, which is initiated by the observance of dark linear defects. Besides, we have shown that on slowly decreasing pressure a new phase can be recovered, which we have attributed to the DZ phase on the basis of the XRD measurements[15] and the broad Raman modes observed resembling a one-phonon density of states, as it is expected in a disordered compound. Furthermore, additional support for the assignment of the new phase to the DZ phase is the considerably decrease of the direct bandgap energy of the new phase with respect to the bandgap in the DC phase discussed in the next section. Therefore, we have shown that the order-disorder DC-to-DR transition in DC-$CdGa_2Se_4$ is irreversible and that the cation ordering cannot be recovered after the transition to the DR phase were all cations and vacancies are totally disordered in cation sites.

2. *Second upstroke*

As already commented, we have obtained a new phase on slowly decreasing pressure to 1.0 GPa from 22 GPa that we have attributed to the DZ phase in agreement with results of Grzechnik *et al*.[15] This result is in contrast with results of Ursaki *et al*.[11] and Mitani *et al*.,[12] who found that the sample remained opaque on decreasing pressure and suggested an irreversible DC-to-DR transition where the sample is quenched in the DR phase at ambient conditions. To know more about the nature of the new phase obtained on downstroke and to help in the assignment of the Raman modes in the new phase, we have performed Raman measurements during a second upstroke.

The evolution of the Raman spectra of DZ-$CdGa_2Se_4$ under pressure up to 16 GPa is shown in Fig. 8. To our knowledge, this is the first study of the evolution of the Raman spectra of DZ-$CdGa_2Se_4$ under pressure. After the first downstroke to 1.0 GPa, we increase again pressure till the sample showed no Raman peaks at pressures above 13.9 GPa due to the decrease of the Raman signal. The Raman spectrum at 1.0 GPa is decomposed into several bands marked by arrows that we have followed under pressure. As pressure increases, the bands shift slightly and at a pressure of 13.9 GPa the Raman spectrum show broad peaks of very small intensity, being the last Raman spectrum taken at 16.4 GPa. Above this pressure, no Raman peaks have been observed, so we have attributed it to the DZ-to-DR phase transition because many binary compounds crystallizing in the zinc blende structure at ambient pressure, such as GaAs, CdSe, etc., undergo a transition to the rock salt structure at

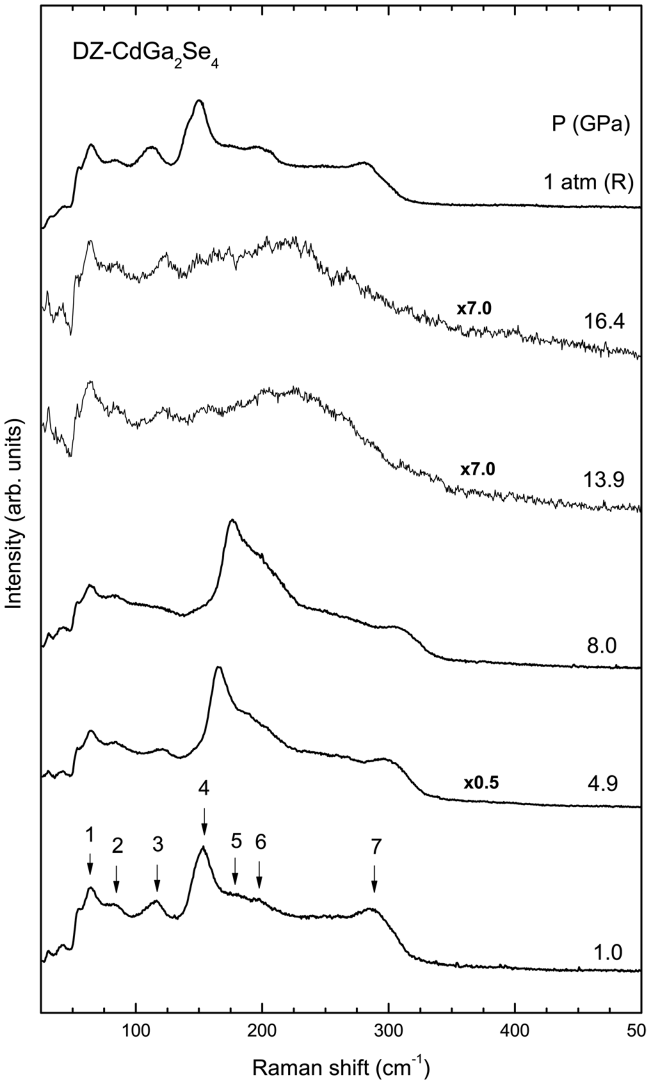

FIG. 8. Room-temperature Raman spectra of DZ-$CdGa_2Se_4$ during the second pressure cycle up to 16.4 GPa and after releasing pressure at ambient pressure (R). Numbers refer to the main peak positions for the disordered zinc blende phase.

high pressure. After the transition of the sample to the DR phase, we decrease slowly pressure and found that the Raman spectrum of the released sample at ambient pressure was similar to that of a DZ phase, thus indicating the reversible nature of the DZ-to-DR phase transition. The reversibility of this pressure-induced disorder-disorder phase transition is consistent with the irreversibility of the pressure-induced order-disorder phase transitions and allow us to explain why the DC or the DS phases of $CdGa_2Se_4$ cannot be obtained on downstroke after complete cation disorder in the DR phase above 20 GPa.

Let us discuss now the nature of the different bands marked by arrows in Fig. 8. In this respect, Fig. 9 shows the pressure dependence of the frequencies of the main peaks in the Raman spectrum of DZ-$CdGa_2Se_4$. The evolution of Raman peak frequencies is practically linear with pressure. The frequencies at zero pressure and the pressure coefficients of the experimental modes in DZ-$CdGa_2Se_4$ are reported in Table III. The high-frequency modes in the DZ phase present a higher linear pressure coefficient than those with lower frequency, and in general we have found that the maximum values of the pressure coefficients are larger in the DC phase than in the DZ phase. Thus, it can be concluded that pressure coefficients of Raman mode frequencies decrease in $CdGa_2Se_4$ as disorder increases.

TABLE III. Experimental Raman-mode frequencies and pressure coefficients observed in disordered zincblende $CdGa_2Se_4$ at room temperature as obtained from fits to the data using $\omega = \omega_0 + aP$ where ω_0 is expressed in cm^{-1} and a in cm^{-1} GPa^{-1}.

Peak	ω_0	a
1	64.7	−0.04
2	82.7	0.23
3	114.6	1.43
4	149.5	3.41
5	177.0	1.07
6	199.5	0.36
7	284.6	2.79

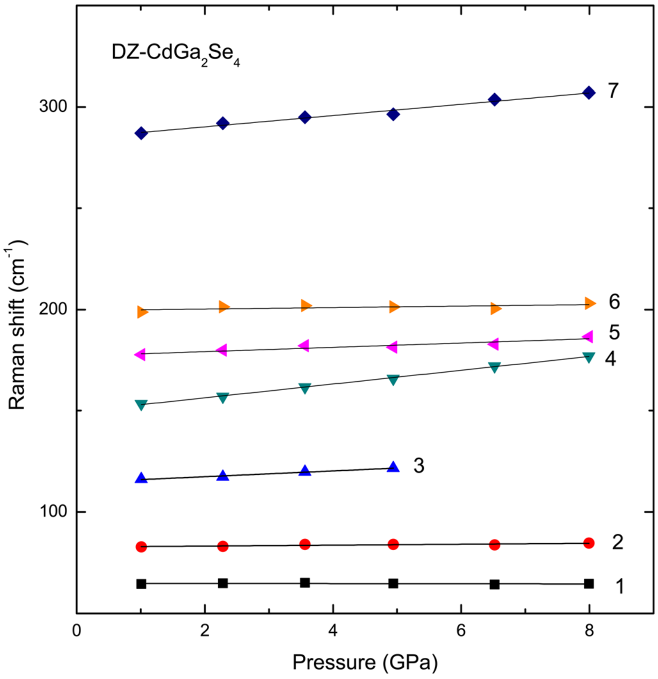

FIG. 9. (Color online) Pressure dependence of the experimental Raman modes in DZ-$CdGa_2Se_4$ during the second pressure cycle. Numbers refer to the main peak positions as indicated in Fig. 8. Solid lines correspond to linear fits to the experimental data.

It can be also noted that the different pressure coefficients of the modes in the DZ phase correlate well with those obtained in the DC phase for modes at similar frequencies. In particular, modes 1 and 2 of the DZ phase are close in energy to E^1 and B^1 modes in the DC phase and show a very small and even negative pressure coefficient as expected for the TA modes of the zinc blende structure at the Brillouin zone edge.[40] Similarly, mode 3 correlates in energy with E^2 and B^2 modes of the DC phase, and it shows a negligible but positive pressure coefficient. This mode is in good agreement with one of the expected LA modes at the Brillouin zone edge of the DZ phase. On the other hand, modes 5 and 6 near 200 cm^{-1} correlate with the frequency of E^3, B^3, and B^4 modes of the DC phase, and they show small positive pressure coefficient as expected for TO modes in the DZ phase. Finally, the broad band marked as 7 near 300 cm^{-1} correlates in frequency with the B^5 mode and shows a large pressure coefficient as expected for the LO modes of the DZ phase. The only difference of the Raman spectrum of DZ-$CdGa_2Se_4$ with respect to common DZ phases in binary semiconductors is the presence of mode 4 in our Raman spectrum. This mode correlates in energy and intensity with the A^1 mode of the DC phase, and we attribute it to a non-polar mode due to the presence of vacancies in the DZ phase that is not common in disordered binary compounds with the zinc blende structure. Mode 4 shows the largest pressure coefficient in the DZ phase in good correlation with the A^1 mode of the DC phase, even larger than mode 7 attributed to LO modes in the DZ phase. This result could be indicative that mode 4 is indeed a TO mode coming from a region of the Brillouin zone with a high density of phonon states in the DZ structure. Note that it is known that most zinc blende-type semiconductors show a decrease in the TO-LO splitting due to the decrease of ionicity with increasing pressure because TO modes show larger pressure coefficients than LO modes.

In summary, our tentative assignments for the nature of the different Raman modes observed in the recovered phase of $CdGa_2Se_4$ after the phase transition to the DR structure are consistent with the one-phonon density of states showing the Raman spectrum that one would expect for the DZ phase and with the expected irreversibility of the pressure-induced order-disorder phase transitions.

B. Optical absorption

1. First upstroke

In addition to Raman scattering measurements during two upstrokes and their corresponding downstrokes, we have performed optical absorption measurements in the same conditions than the Raman ones. Figure 10 shows the optical absorption edge of DC-$CdGa_2Se_4$ at different pressures up to 16 GPa. The appearance of dark linear defects above 14 GPa, as commented in the previous section, leads to strong optical

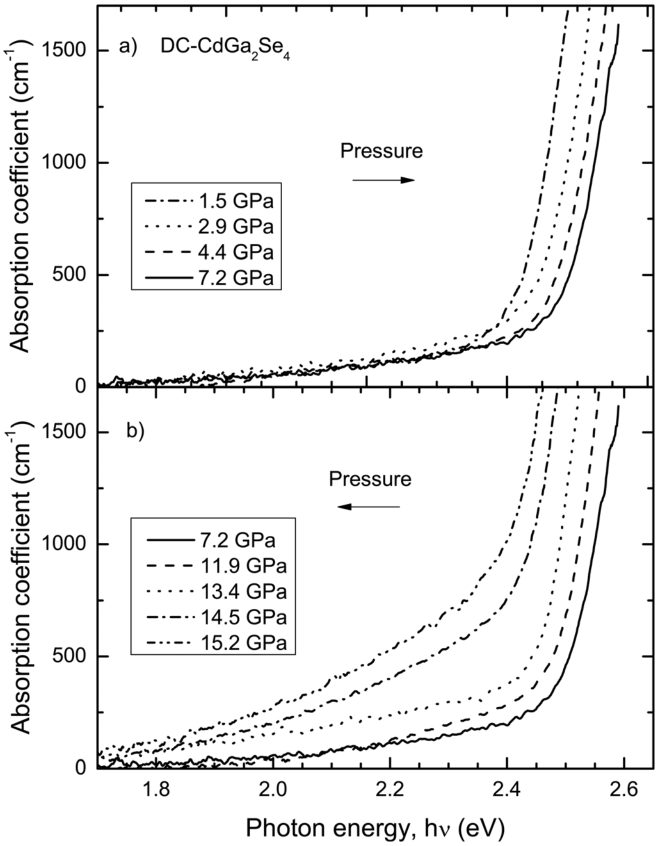

FIG. 10. Absorption edge of DC-CdGa$_2$Se$_4$ on increasing pressure up to 7.2 GPa (a) and from 7.2 up to 16 GPa (b).

scattering and prevents the correct measurement of the optical absorption edge above 16 GPa. It can be observed that the edge shifts to higher energies below 8 GPa, and it shifts to lower energies from 8 GPa till 16 GPa. In our previous work,[16] we explained that the optical absorption edge of DC-CdGa$_2$Se$_4$ and DC-HgGa$_2$Se$_4$ was of direct character and that the direct bandgap shows a strong non-linear pressure dependence at low pressures. Figure 11 shows the pressure dependence of the experimentally estimated direct bandgap energy (circles) in DC-CdGa$_2$Se$_4$, as obtained by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ versus $h\nu$ plot to zero absorption. The strong non-linear pressure dependence of the direct bandgap energy of DC-CdGa$_2$Se$_4$ up to 8 GPa was confirmed by theoretical *ab initio* calculations (see solid line in Fig. 11). In our previous work,[16] we suggested that the strong nonlinear pressure dependence of the direct bandgap is a general feature common to all OVCs due to a conduction band anticrossing at the Γ point of the Brillouin zone caused by two facts: (i) the presence of ordered vacancies in adamantine OVCs and (ii) the doubling of the unit cell along the *c* axis with respect to the zinc blende structure.

In Fig. 11 it can be observed that the direct bandgap energy in DC-CdGa$_2$Se$_4$ increases with a pressure coefficient of 36 ± 4 meV GPa^{-1} at low pressures, while at pressures above 11 GPa, the bandgap energy decreases with a pressure coefficient of -26 ± 3 meV GPa^{-1}. The strong decrease of the direct bandgap above 6-8 GPa cannot be accounted for by our theoretical calculations of the electronic structure, and we think that the reason for the disagreement between experiment and theory above this pressure range is that the disorder process that begins above 6-8 GPa leads to a decrease of the experimental bandgap that is not accounted for by our calculations that did not include cation disorder in the DC structure.

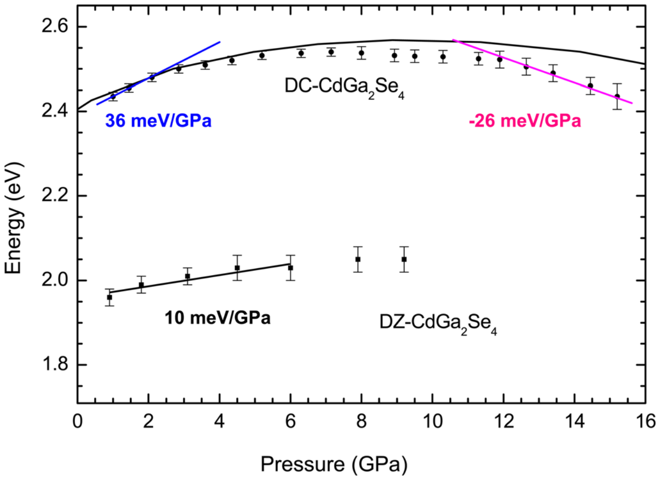

FIG. 11. (Color online) Pressure dependence of the bandgap energy in CdGa$_2$Se$_4$. Circles with error bars correspond to experimental values for the DC phase. Squares with error bars correspond to experimental values for the DZ phase. Theoretical calculations of the direct bandgap for DC phase are shown in solid line. Values of pressure coefficients of the direct bandgap at room pressure and at high pressure are also shown. All calculated energies are upshifted to match the experimental direct bandgap at room pressure.

To understand the decrease of the direct bandgap in DC-CdGa$_2$Se$_4$ above 6-8 GPa, we must recall that the decrease of the direct bandgap on increasing disorder has been reported earlier in other OVCs. In particular, a smaller direct bandgap (by 0.2 eV) has been found in disordered β-CdIn$_2$Se$_4$ than in the ordered α modification.[41] Some authors have attributed this bandgap decrease to band tailing of the conduction band as a consequence of disorder at cation sites because the lowermost conduction band is typically formed by s and d cation states with some p anion hybridization. However, it must be recalled that the band tailing typically occurs at low absorption values (<500 cm^{-1}) as an extension of the absorption edge to low energies and can be clearly seen above 12 GPa in DC-CdGa$_2$Se$_4$ (see Fig. 10). The band tailing can occur either because of cation disorder or by the appearance of scattering centers due to the presence of the dark linear defects that are precursors of the DC-to-DR phase transition. However, the decrease of the direct bandgap, obtained from extrapolation of the high-energy region of the optical absorption coefficient (>1000 cm^{-1}), cannot be attributed to band tailing. In fact, we showed in a recent paper that there is a strong non-linear pressure coefficient of the direct bandgap in DC-CdGa$_2$Se$_4$ and in all OVCs.[16] However, the strong decrease of the direct bandgap measured in DC-CdGa$_2$Se$_4$ above 6-8 GPa is even stronger than theoretically predicted. We think this is a clear evidence of the disorder at cation sites taking place in DC-CdGa$_2$Se$_4$ because a decrease of the direct bandgap is expected to occur at the DC-to-DS transition. In summary, the comparison between measurements and *ab initio* calculations shown in Fig. 11 allows us to estimate the pressures at which the disorder processes begin in OVCs. In particular, our absorption measurements in DC-CdGa$_2$Se$_4$ suggest that the cation disorder process would start at about 6-8 GPa. Note that the small but progressive decrease in energy of the experimental bandgap energy above 6-8 GPa results in a difference with respect to the theoretical values for the DC phase which amounts around 0.1 eV at 16 GPa. This bandgap energy difference is consistent with a gradual phase transition from the DC to the DS structure in good agreement with our Raman scattering measurements.

To check the reversibility of the order-disorder processes, we have measured the optical absorption edge of CdGa$_2$Se$_4$ on downstroke from 22 GPa until almost ambient pressure (0.9 GPa). Note that at 22 GPa, the sample was completely opaque as it should be in the metallic DR phase, thus confirming that the DC-to-DR phase transition was completely accomplished. We have found that the sample becomes transparent again below 4 GPa, thus showing a strong hysteresis in the phase transition. Furthermore, we have found that the direct bandgap of the recovered sample at 0.9 GPa, and attributed to the DZ phase, was more than 0.4 eV smaller than that of the initial sample in the DC phase (see Fig. 11). The decrease of the bandgap can be directly noted by the redshift color of the sample—initially it was orange and after recovering transparency, it was red. This decrease of the bandgap energy is attributed to cation and vacancy disorder at cation sites of the initial DC structure leading to the DZ phase. In fact, a strong decrease of the direct bandgap in going from ordered chalcopyrite structure to DZ structure has been found in several chalcopyrite-type compounds.[42] Besides, a similar but smaller decrease of the bandgap was also experimentally found in CdGa$_2$Te$_4$ where the disorder at cation sites causes the decrease of the bandgap energy from 1.5 eV in the ordered DC structure to 1.4 eV in the DZ phase.[3] Therefore, we interpret that the strong decrease of the direct bandgap in CdGa$_2$Se$_4$ on downstroke is an evidence of the formation of the DZ phase due to the non-reversibility of the pressure-induced order-disorder processes in DC-CdGa$_2$Se$_4$.

Furthermore, the decrease of the direct bandgap in disordered phases of OVCs can be attributed to the change of the electronic structure caused by a change of the structure symmetry and unit-cell volume; i.e., it could be likely due in part to a change in the electronic band structure and in part to the larger volume per formula unit in the disordered structures than in ordered ones. In particular, the decrease of the bandgap in DC-CdGa$_2$Se$_4$ above 6-8 GPa is due to the progressive transformation of the DC phase into the DS phase because a small decrease of the direct bandgap (0.1-0.3 eV) on going from DC to DS is expected because of the slightly larger c/a ratio and volume in the DS phase than in the DC phase. On the other hand, the strong decrease of the bandgap in DZ-CdGa$_2$Se$_4$ with respect to DC-CdGa$_2$Se$_4$ could be strongly contributed by the larger volume per formula unit in the DZ phase than in the DC phase.[15] The larger the volume per formula unit, the larger the cation-anion bond distances resulting in less hybridization and consequently in a smaller direct bandgap. This effect is just the opposite of increasing pressure because increasing pressure usually leads to the decrease of the cation-anion bond distances resulting in an increase of the direct bandgap.

The pressure dependence of the optical absorption edge in tetrahedrally coordinated DZ-CdGa$_2$Se$_4$ is shown in Fig. 12. These measurements are obtained during a second upstroke up to 17 GPa after recovering the sample at 0.9 GPa. It has been observed that DZ-CdGa$_2$Se$_4$ undergoes a phase transition at about 14 GPa. At this pressure, the sample becomes opaque so we consider that the high-pressure structure is the same octahedrally coordinated DR structure with metallic character previously observed during the first upstroke above 18 GPa. It is interesting to note that the optical absorption spectra of DZ-CdGa$_2$Se$_4$ does not show strong band tailing despite the DZ phase has a total cation-vacancy disorder. This gives support to the strong appearance of band tailing above 11 GPa in DC-CdGa$_2$Se$_4$ [see Fig. 10(b)] as a consequence of the appearance of dark linear defects precursors of the DC-to-DR phase transition above that pressure. In this respect, we consider that cation disorder in the DZ phase represents a small contribution to band tailing responsible for the less steep optical absorption edge at intermediate absorption values in DZ than in DC-CdGa$_2$Se$_4$.

From the optical absorption edge of the DZ structure, we have obtained the direct bandgap energy as a function of pressure by extrapolating the linear fit of the high-energy part of the $(\alpha h\nu)^2$ versus hν plot to zero absorption (square symbols in Fig. 11). We have only obtained estimated values for the direct bandgap energy of DZ-CdGa$_2$Se$_4$ up to about 10 GPa because at higher pressures, the absorption edge has a big tail due to dark linear defects, which are precursors of the DZ-to-DR phase transition, and keep us from obtaining the bandgap energy by extrapolation with reasonable accuracy. The pressure coefficient of the direct bandgap of DZ-CdGa$_2$Se$_4$ at ambient pressure is estimated from a linear fit to be around 10 ± 2 meV·GPa^{-1}. This pressure coefficient for the DZ phase is much smaller than that of the DC phase at ambient pressure (36 meV·GPa^{-1}) and much smaller than the pressure coefficients of binary zinc blende-type compounds, in particular zinc blende CdSe (37 meV·GPa^{-1}).[43,44] We must note that this pressure coefficient is also much smaller than the pressure coefficient theoretically calculated by us for DS-CdGa$_2$Se$_4$ (31 meV·GPa^{-1}) using the ordered cation DS structure corresponding to model 1 in Table II.[16] Therefore the small direct bandgap pressure coefficient of the

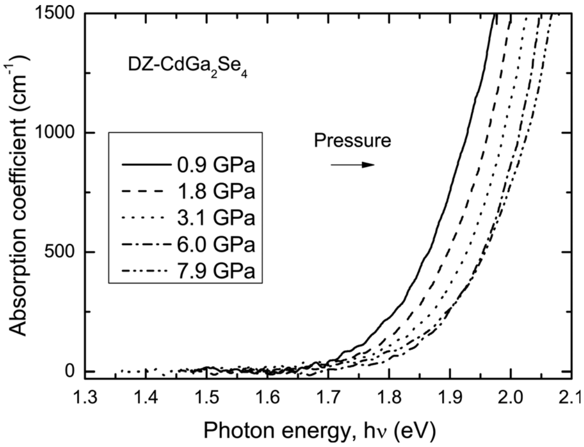

FIG. 12. Absorption edge of DZ-CdGa$_2$Se$_4$ on increasing pressure.

recovered phase gives us confidence to assign this structure to the DZ phase instead to the DC or DS phases.

The reason for the small pressure coefficient of the direct bandgap in DZ-$CdGa_2Se_4$ and other OVCs with DZ phase can be understood on the basis of the structure of the conduction band (CB) of OVCs and the large absolute pressure coefficient of the valence band.[16] We showed in a previous work that the CB of adamantine OVCs consisted of two low-energy CBs at the Brillouin zone center (Γ) with the same symmetry named first and second CBs.[16] In DC-$CdGa_2Se_4$, the first and lowermost CB is mostly contributed by the Ga and Cd cations at *2c* and *2d* Wyckoff sites while the second CB is mainly contributed by the Ga cations at *2a* Wyckoff sites. The different contribution of cations to the two CBs yielded a very large absolute pressure coefficient of the first CB and a rather small absolute pressure coefficient of the second CB [see Fig. 5(a) in Ref. 16]. These two low-energy CBs at DC phase have the same symmetry and come from the doubling of the zinc blende electronic band structure along the *c* axis in the DC structure [see Fig. 1(a)]. Consequently, these two CBs should merge into one single band in the DZ phase, thus leading to a lowermost CB with an absolute pressure coefficient that will be considerably smaller than that of the first CB of the DC phase. Our theoretical calculations[16] yield absolute pressure coefficients of 280 and 140 meV·GPa^{-1} for the first and second CBs in DC-$CdGa_2Se_4$, respectively, while the absolute pressure coefficient of the valence band is 246 meV·GPa^{-1}. With these numbers and imposing the experimental value of the direct bandgap in the DZ phase (10 meV·GPa^{-1}), one obtains that the CB of the DZ phase at the Γ point of the Brillouin zone would be composed almost of 83% and 17% of first and second CB of the DC phase, respectively.

Finally, we are going to give new arguments supporting the assignment of the recovered phase to the DZ phase on the basis of XRD, Raman scattering, and optical absorption measurements. It can be argued that several candidate phases could lead to the measured Raman spectrum of the recovered sample, which resembles a one-phonon density of states and exhibits a rather small bandgap. One possibility is that the recovered sample has a DC or DS structure; i.e., showing a reversible DC-to-DR transition, but where the initial single crystal becomes a polycrystalline sample with grains of nanometric size after the pressure treatment. In that case, Raman selection rules would be relaxed in a way that a Raman measurement shows not only the phonons at the Γ point of the Brillouin zone but an average of the phonons of the whole first Brillouin zone. This case has been observed to occur in several zinc blende-type semiconductors like CdSe;[45] however, the optical absorption edge of nanometric semiconductors is blueshifted with respect to the bulk. This is in contrast with our optical absorption results showing a decrease of the direct bandgap in the recovered sample. Therefore, we can exclude the existence of DC or DS phases of nanometric domain in our recovered samples. Another possibility is that the recovered sample belongs to one of the DS structures commented in the previous section, thus exhibiting a partial cation disorder already present before the transition to the DR phase. If this was the case, in most cases, we expected a slightly broader Raman spectrum than that of the DC phase, like it occurs in DS-$ZnGa_2Se_4$ but much less broad than that observed in the recovered sample. This would be the case if vacancies are still ordered (models 1-3) or with a slight cation and vacancy disorder (models 4 and 5). Furthermore, if these were the case, we would expect a slight decrease of the direct bandgap (around 0.1-0.2 eV) and not of 0.4 eV as observed in the recovered sample. Therefore, we can exclude the possibility that the recovered sample shows a DS structure. Consequently, we are finally faced to consider that the recovered sample could have either a DCA structure with a large cation and vacancy disorder like those of models 6-10 of Table II, where disorder affects to the two planes of cations perpendicular to the tetragonal *c* axis, or a DZ structure with a total cation and vacancy disorder. In either of these cases, we would expect very few Raman-active modes and a very broad Raman spectrum with overlapped bands showing the one-phonon density of states that would be much broader for DZ than for DCA phases because of the larger disorder in the former structure. Besides, in all these disordered structures, we would expect a strong decrease of the direct bandgap as already observed experimentally with a slightly larger decrease of the direct bandgap in the DZ phase than in the DCA phases. Therefore, due to the lack of previous Raman scattering and optical absorption measurements in both DCA or DZ phases in different ternary compounds like chalcopyrites and other OVCs, we cannot assure that the recovered phase is a DZ or a DCA phase. However, there are two arguments that lead us to propose the recovered phase as the DZ phase. On one hand, the DCA phase is a layered phase that has some degree of cation-vacancy ordering, unlike the DZ with a total cation-vacancy disorder. In this respect, the expected irreversibility of the pressure-induced order-disorder phase transitions suggests that the slightly ordered DCA phase cannot be recovered from the DR phase with a total cation-vacancy disorder. On the other hand, the availability of high-pressure XRD measurements in $CdGa_2Se_4$ and the observation of the DZ phase on downstroke[15] leads us to assume that the recovered phase of this compound after the phase transition to the DR phase is the DZ phase. Note that the DZ structure is cubic while the DCA structure is tetragonal, therefore XRD could be able to distinguish between the two structures. In any case, more detailed XRD measurements in pressure-treated OVCs recovered from the DR phase should be done to confirm whether the recovered phase is a DZ or a DCA phase.

V. CONCLUSIONS

We have performed Raman scattering and optical absorption measurements in defect chalcopyrite $CdGa_2Se_4$ up to 22 GPa during two upstrokes and their corresponding downstrokes, which have been complemented with *ab initio* electronic structure and lattice dynamics calculations. As regards the first upstroke, our Raman scattering measurements of DC-$CdGa_2Se_4$ complemented with lattice dynamics calculations have allowed us to assign and discuss the symmetries of the different Raman-active modes observed. Besides, our Raman measurements show evidence of the activation of pressure-induced disorder by the increase of the

FWHM of most Raman peaks and the decrease of the intensity of the A^2 Raman mode above 6–8 GPa. These results have led us to conclude that above this pressure range, a cation disorder occurs resulting in a partial and progressive transformation from the DC to the DS phase (model 2 or 3 in Table II) on increasing pressure. This partial transformation is prior to the transition to the DR structure above 18 GPa that is preceded by the appearance of dark linear defects that are precursors of the phase transition and lead to a considerable decrease of the intensity of all Raman modes above 14-16 GPa. We have found no signature supporting a pressure-induced two-stage process of cation disorder leading from the DC to the DZ structure in contrast with the predictions of this type of process on increasing temperature.

As regards our optical absorption measurements during the first upstroke, we have shown that the direct bandgap energy in DC-$CdGa_2Se_4$ shows a non-linear pressure dependence that is well accounted for by our calculations at low pressures.[16] However, at pressures beyond 6–8 GPa, there is a lack of agreement between the theoretical and experimental pressure dependence of the direct bandgap energy. We have interpreted the decrease of the experimental direct bandgap with respect to the theoretical value as an evidence of the pressure-induced disorder taking place at the cation sites as already mentioned in the previous paragraph. The reasons for our interpretation are: (i) our *ab initio* calculations do not consider the cation-vacancy disorder at any pressure and (ii) it is known that disorder induces a decrease of the bandgap energy in related compounds like chalcopyrites. Consequently, the comparison of optical absorption measurements with *ab initio* electronic structure calculations has allowed us to estimate the pressure at which the cation-vacancy disorder process begins in $CdGa_2Se_4$.

As regards the downstroke and second upstroke, we have slowly decreased pressure from 22 GPa, where sample is opaque due to the metallic character of the DR phase, and we have shown that the sample becomes transparent below 4 GPa. The Raman spectrum of the recovered sample below 4 GPa did not resemble that of the initial DC phase because it consists of very broad Raman features that resemble a first-order one-phonon density of states. We have interpreted all these results as evidence that on decreasing pressure the sample is a highly disordered semiconducting phase that we have tentatively attributed to the disordered zinc blende (DZ) phase in agreement with XRD measurements.[15] This disordered phase is formed due to the irreversibility of the order-disorder process after transition to the DR structure. The pressure coefficients of the direct bandgap energy and of the Raman-active modes in the DZ phase were measured in a second upstroke. The small bandgap energy and pressure coefficient of the bandgap energy as well as the nature and pressure coefficients of the features in the Raman spectrum of the DZ phase were also discussed.

Furthermore, after transiting the sample from the DZ to the DR phase, we measured the optical and vibrational properties during the second downstroke finding that the sample returned again to the DZ phase; thus confirming the metastable character of this disordered structure on downstroke.

We hope that the present study will stimulate further studies in AB_2X_4 OVCs under pressure. In particular, XRD measurements on decreasing pressure would be desirable as well as theoretical calculations of electronic band structure and lattice dynamics of the proposed disordered phases to fully understand the order-disorder processes and to confirm the nature of the recovered phase.

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