High-pressure x-ray diffraction study on the structure and phase transitions of the defect-stannite ZnGa$_2$Se$_4$ and defect-chalcopyrite CdGa$_2$S$_4$

D. Errandonea,$^1,a)$ Ravi S. Kumar,$^2$ F. J. Manjón,$^3$ V. V. Ursaki,$^4$ and I. M. Tiginyanu$^4$

$^1$MALTA Consolider Team, Departamento de Física Aplicada-ICMUV, Fundación General de la Universidad de Valencia, Edificio de Investigación, c/Dr. Moliner 50, 46100 Burjassot, Valencia, Spain
$^2$High Pressure Science and Engineering Center, Department of Physics and Astronomy, University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas, Nevada 89154-4002, USA
$^3$MALTA Consolider Team, Departamento de Física Aplicada-IDF, Universitat Politècnica de València, Cno. de Vera s/n, 46022 València, Spain
$^4$Institute of Applied Physics, Academy of Sciences of Moldova, 2028 Chisinau, Moldova

(Received 17 April 2008; accepted 25 July 2008; published online 25 September 2008)

X-ray diffraction measurements on the sphalerite-derivatives ZnGa$_2$Se$_4$ and CdGa$_2$S$_4$ have been performed upon compression up to 23 GPa in a diamond-anvil cell. ZnGa$_2$Se$_4$ exhibits a defect tetragonal stannite-type structure ($I4_2m$) up to 15.5 GPa and in the range from 15.5 to 18.5 GPa the low-pressure phase coexists with a high-pressure phase, which remains stable up to 23 GPa. In CdGa$_2$S$_4$, we find that the defect tetragonal chalcopyrite-type structure ($I4$) is stable up to 17 GPa. Beyond this pressure a pressure-induced phase transition takes place. In both materials, the high-pressure phase has been characterized as a defect-cubic NaCl-type structure ($Fm\bar{3}m$). The occurrence of the pressure-induced phase transitions is apparently related with an increase in the cation disorder on the semiconductors investigated. In addition, the results allow the evaluation of the axial compressibility and the determination of the equation of state for each compound. The obtained results are compared to those previously reported for isomorphic digallium selenides.

Finally, a systematic study of the pressure-induced phase transition in 23 different sphalerite-related $ABX_2$ and $ABX_4$ compounds indicates that the transition pressure increases as the ratio of the cationic radii and anionic radii of the compounds increases. © 2008 American Institute of Physics. [DOI: 10.1063/1.2981089]

I. INTRODUCTION

Zinc digallium selenide (ZnGa$_2$Se$_4$) and cadmium digallium sulphide (CdGa$_2$S$_4$) are tetrahedrally coordinated $A^\text{II}B^\text{III}_2X^\text{VI}_4$ defective compounds, the structure of which is still contradictory discussed in literature. While some studies suggest a defect-chalcopyrite structure ($I4$) others report a defect-stannite structure ($I4_2m$) for these compounds. Both structures are tetragonally and structurally related to the cubic sphalerite structure ($F\bar{4}3m$), commonly known as zinc blende, with only differences arising due to slight deviations on the atomic positions of the anions. This family of semiconductors is of interest as possible infrared-transmitting window materials. This is also applied in various nonlinear optical devices and as gyrotropic media in narrow-band optical filters. In addition, these compounds are promising optoelectronic materials due to their high values of nonlinear susceptibility, optical activity, intense luminescence, and high photosensitivity. Some compounds such as CdGa$_2$Se$_4$ and CdAl$_2$S$_4$ have already found practical applications as tunable filters and ultraviolet photodetectors.$^{1,2}$

High-pressure studies on $ABX_2$ and $ABX_4$ compounds are receiving increasing interest in the past years. In particular, these materials have been extensively studied by the Raman spectroscopy$^{3-6}$ because of pressure-induced phase transitions. However, the structure of the high-pressure phases has been so far characterized only for two compounds, CdGa$_2$Se$_4$ (Ref. 7) and MnGa$_2$Se$_4$. In both materials the high-pressure phase has been determined as a cubic NaCl-type structure.

In the present work, we report angle dispersive x-ray diffraction (ADXRD) measurements performed on ZnGa$_2$Se$_4$ and CdGa$_2$S$_4$ as a function of pressure in a diamond-anvil cell (DAC) at room temperature up to 23 GPa. From these experiments, we have determined the effect of pressure on the lattice parameters and atomic positions, as well as observed pressure-driven structural phase transitions. In both compounds, the high-pressure phase has been characterized and assigned to a defect NaCl-type structure. We also determined the equation of state (EOS) of CdGa$_2$S$_4$ and ZnGa$_2$Se$_4$ and further discuss the systematics of pressure-induced phase transitions on sphalerite derivatives.

II. EXPERIMENT

Single crystals of CdGa$_2$S$_4$ and ZnGa$_2$Se$_4$ were grown by chemical vapor method using iodine as a transport agent. The as grown crystals represent triangular prisms with mirror surfaces. Chemical and structural analyses have shown the stoichiometric composition of the crystals and no spurious phases were observed. ADXRD experiments were carried out at room temperature under compression up to 23 GPa using a DAC at sector 16-IDB of the HPCAT, at the Advanced
III. RESULTS AND DISCUSSION

A. The structure of CdGa$_2$S$_4$ and ZnGa$_2$Se$_4$

ZnGa$_2$Se$_4$ has been reported to have either a tetragonal defect-chalcopyrite ($I\bar{4}$, $Z=2$) or a tetragonal defect-stannite ($I\bar{4}2m$, $Z=2$) structure. Both structures are shown in Fig. 1. Recent Raman measurements supported the space group $I\bar{4}$ for ZnGa$_2$Se$_4$, but accurate neutron diffraction studies unambiguously established that it belongs to the space group $I\bar{4}2m$. Our experiments agree with the conclusions drawn from the neutron experiments. After a Rietveld refinement of an x-ray diffraction pattern collected at ambient pressure (0.1 MPa) outside the DAC the following structural parameters for defect-stannite ZnGa$_2$Se$_4$ were obtained: $a=5.512(3)$ Å and $c=10.963(6)$ Å. The residuals of the refinement are $R_p^2=2.52\%$, $R_{wp}=3.97\%$, and $R_F=2.07\%$. The atomic positions obtained for the defect-stannite structure are summarized in Table I. According to the site occupation fraction (SOF) obtained in the structural refinement, a partial cation order is present in ZnGa$_2$Se$_4$. However, since Ga and Zn have nearly equal x-ray scattering factors, it is hard to distinguish between this model with others considering a complete cation order (Zn at 2$a$ and Ga at 4$d$) or a complete cation disorder (Zn:Ga=1:3:2:3 at 2$a$ and 4$d$). Indeed these models resulted in slightly larger R-factors if considered for the structural refinement than the partial ordering model (see atomic positions in Table I). Nevertheless, based upon this fact and the conclusions drawn by Hanada, we think it can be concluded that the structure of ZnGa$_2$Se$_4$ is defect stannite as summarized in Table I. This type of structure is observed in the minerals famatinite (Cu$_2$Sn$_4$S$_8$) and stannite (Cu$_3$FeSnS$_4$). According to the partial cation ordering model, in ZnGa$_2$Se$_4$, half of the Ga atoms occupy the position of Fe in stannite, the other half and the Zn atoms occupy the position of Cu and the Se atoms are located at the position of S. The structure of ZnGa$_2$Se$_4$ is called defect stannite (some authors call it defect famatinite) because the Sn atoms (located at 2$b$ in stannite) are replaced by vacancies in this compound. Further, in ZnGa$_2$Se$_4$ the Zn and Ga cations and the vacancies are in tetrahedral coordination, but these tetrahedra differ in dimension and bond angles. For the Ga atoms located at 2$a$, the Ga–Se bond distance is 2.42 Å and for the Ga and Zn atoms located at 4$d$, the Ga(Ga)–Se bond distance is 2.44 Å. The vacancy-Se distance is 2.24 Å. It is important to note that the cation-anion bonds are close to those found in ZnSe (2.45 Å) (Ref. 18) and in the high-temperature phase of G$_3$Sb$_2$S$_6$ (2.42 Å). However, the vacancy-anion distance is much shorter due to the fact that the Se atoms are displaced from the ideal $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ toward the vacancy.

Regarding CdGa$_2$S$_4$, it is accepted that it has a defect-chalcopyrite structure ($I\bar{4}$) in which one cation site is also vacant (at 2$d$). In a similar way to ZnGa$_2$Se$_4$, we also analyzed CdGa$_2$S$_4$ at ambient conditions outside the DAC. Rietveld refinement of the x-ray diffraction pattern collected at ambient conditions provided the following structural parameters for the defect-chalcopyrite structure of CdGa$_2$S$_4$: $a=5.536(3)$ Å and $c=10.160(6)$ Å with refinement residuals $R_p^2=2.52\%$, $R_{wp}=3.97\%$, and $R_F=2.07\%$. The atomic positions obtained for the defect-chalcopyrite structure are summarized in Table I. According to the site occupation fraction (SOF) obtained in the structural refinement, a partial cation order is present in CdGa$_2$S$_4$. However, since Ga and Cd have nearly equal x-ray scattering factors, it is hard to distinguish between this model with others considering a complete cation order (Cd at 2$a$ and Ga at 4$d$) or a complete cation disorder (Cd:Ga=1:3:2:3 at 2$a$ and 4$d$). Indeed these models resulted in slightly larger R-factors if considered for the structural refinement than the partial ordering model (see atomic positions in Table I). Nevertheless, based upon this fact and the conclusions drawn by Hanada, we think it can be concluded that the structure of CdGa$_2$S$_4$ is defect chalcopyrite as summarized in Table I. This type of structure is observed in the minerals famatinite (Cu$_2$Sn$_4$S$_8$) and chalcopyrite (Cu$_2$FeSnS$_4$). According to the partial cation ordering model, in CdGa$_2$S$_4$, half of the Ga atoms occupy the position of Fe in chalcopyrite, the other half and the Cd atoms occupy the position of Cu and the Se atoms are located at the position of S. The structure of CdGa$_2$S$_4$ is called defect chalcopyrite (some authors call it defect famatinite) because the Sn atoms (located at 2$b$ in chalcopyrite) are replaced by vacancies in this compound. Further, in CdGa$_2$S$_4$ the Cd and Ga cations and the vacancies are in tetrahedral coordination, but these tetrahedra differ in dimension and bond angles. For the Ga atoms located at 2$a$, the Ga–Se bond distance is 2.42 Å and for the Ga and Cd atoms located at 4$d$, the Ga(Ga)–Se bond distance is 2.44 Å. The vacancy-Se distance is 2.24 Å. It is important to note that the cation-anion bonds are close to those found in CdSe (2.45 Å) (Ref. 18) and in the high-temperature phase of G$_3$Sb$_2$S$_6$ (2.42 Å). However, the vacancy-anion distance is much shorter due to the fact that the Se atoms are displaced from the ideal $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ toward the vacancy.

TABLE I. Atomic positions and SOF refined for ZnGa$_2$Se$_4$ at ambient pressure. Defect-stannite structure, space group: $I\bar{4}2m$, $Z=2$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>SOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>2$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Ga</td>
<td>4$d$</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn</td>
<td>4$d$</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
<td>0.5</td>
</tr>
<tr>
<td>Vacancy</td>
<td>2$b$</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>Se</td>
<td>8$i$</td>
<td>0.264(8)</td>
<td>0.264(8)</td>
<td>0.117(4)</td>
<td>1</td>
</tr>
</tbody>
</table>

Phonon Source (APS). CdGa$_2$S$_4$ was studied with an incident monochromatic wavelength of 0.36806 Å and ZnGa$_2$Se$_4$ with a wavelength of 0.41521 Å. The samples used in the experiments were prepressed pellets prepared using a finely ground powder obtained from the as grown single crystals. These pellets were loaded in a 130 μm hole of a rhenium gasket in a Mao–Bell-type DAC with diamond-culet sizes of 350 μm. A few ruby grains were also loaded with the sample for pressure determination, and silicone oil was used as pressure-transmitting medium. The monochromatic x-ray beam was focused down to 10 μm$^2$ using Kickpatrick–Baez mirrors. The images were collected using a MAR345 image plate located 380 mm away from the kickpatrick–baez mirrors. The collected images were integrated and corrected for distortions using FIT2D. The structure refinements were performed using the POWDERCELL (Ref. 13) program package.

FIG. 1. (Color online) (a) Defect-chalcopyrite structure of CdGa$_2$S$_4$. Small blue circles: S, large red circles: Cd, and large magenta circles: Ga. (b) Defect-stannite structure of ZnGa$_2$Se$_4$. Small blue circles: Se, large red circles: Ga, and large magenta circle: Ga and Zn atoms (SOF=0.5 for each one).
Errandonea et al.  


\[ R_F = 2.02\%, \quad R_{wp} = 2.87\%, \quad \text{and} \quad R_F = 1.67\%. \]

The lattice parameters obtained agree with the values available in literature. The atomic positions determined in the structural refinement are summarized in Table II. The structure observed for CdGa_2S_4 is typical to the mineral kesterite (Cu_2ZnSnS_4).\(^{17}\) In the case of CdGa_2S_4, half of the Ga atoms occupy the position of Sn as in kesterite, the other half and the Cd atoms occupy the position of Cu, while the S atoms stay at the same position. In this case, the vacancies occupy the position of Zn. The structure of CdGa_2S_4 is called defect chalcopyrite because it can be constructed from the chalcopyrite structure of CuGaS_2 (\(I4\bar{2}d\)) (Ref. 21) by doubling the formula unit and replacing Cu by Cd and a vacancy to maintain the valence. In CdGa_2S_4 the Cd and Ga cations and the vacancies are in tetrahedral coordination, but these tetrahedra differ in dimension and bond angles. We found the Cd–S bond distance to be 2.52 Å, the Ga–S distance to be 2.33 Å (for the Ga atoms at 2b) and 2.29 Å (for Ga atoms at 2c). The vacancy-S distance was found to be 2.22 Å. The Cd–S distance is exactly the same as in CdS (Ref. 22) and the Ga–S distances are close to the ones reported for Ga_2S_3 (2.22 Å).\(^{23}\)

**B. Pressure-induced phase transitions**

A summary of the results obtained in the high-pressure x-ray diffraction experiments for ZnGa_2Se_4 and CdGa_2S_4 is shown in Figs. 2 and 3, respectively. In ZnGa_2Se_4, we did not observe any substantial change in the x-ray diffraction patterns up to 10.37 GPa. At this pressure we found that most of the diffraction peaks become broader. The peak broadening increases with pressure beyond 10.37 GPa. This broadening can be clearly seen in Fig. 2 looking at the peak located near 2\(\theta\) = 7.6° — the (112) reflection — whose full width at half maximum is smaller than 0.2° below 10.37 GPa, but it becomes 0.3° at 10.37 GPa and 0.4° at 17.5 GPa. A similar phenomenon has been observed around 10 GPa in Raman measurements.\(^{3,5}\) Peak broadening in both cases could be related with an increase in the crystalline disorder induced by pressure. It could be also related to nonhydrostatic effects due to the use of silicone oil as pressure-transmitting medium.\(^{11}\) These effects cannot be neglected beyond 10 GPa. However, as we will show later, the observed reduction in the anion distortion parameter \(\sigma_0\) under compression supports the first hypothesis. At 15.5 GPa we observe the appearance of new diffraction peaks. The intensity of these peaks is found to increase with pressure. They are indicated by asterisks in the pattern collected at 17.5 GPa. At 18.5, the intensity of the peaks assigned to the low-pressure phase decreased considerably and the new peaks became dominant in the diffraction pattern. The peaks corresponding to the low-pressure phase disappeared at 19.2 GPa. All these changes indicated the occurrence of a pressure-driven phase transition. We have located the onset of the transition at 15.5 GPa and a coexistence of the low- and high-pressure phases was noticed up to 18.5 GPa. The transition is complete at 19.2 GPa. Upon further compression the high-pressure phase appears to remain stable up to 23 GPa, the highest pressure reached in our experiments. On pressure release, we reduced the pressure in three steps; from 23 GPa to 14.7 GPa, 2 GPa, and ambient pressure, respectively. Apparently the phase transition is irreversible since the diffraction pattern, collected on the sample recovered at ambient pressure, resembled very much the diffraction patterns of the high-pressure phase. In Raman experiments, a decrease in the intensity of Raman signal has been detected beyond 14.7 GPa and a total disappearance at 18.9 GPa.\(^{3,5}\) On decompre-

---

### Table II. Atomic positions and SOF refined for CdGa_2S_4 at ambient pressure. Defect-chalcopyrite structure, space group: \(I4, Z=2\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>SOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Ga</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>Ga</td>
<td>2c</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
<td>1</td>
</tr>
<tr>
<td>Vacancy</td>
<td>2d</td>
<td>0</td>
<td>1/2</td>
<td>3/4</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>8i</td>
<td>0.271(8)</td>
<td>0.261(8)</td>
<td>0.140(4)</td>
<td>1</td>
</tr>
</tbody>
</table>
CdGa$_2$Se$_4$, the high-pressure phases of ZnGa$_2$Se$_4$ and shown together with the refined patterns. CdGa$_2$S$_4$ have a higher-symmetry cubic NaCl-type structure. We have identified the phase transition pressure as 11.4 GPa. Raman measurements reported for CdGa$_2$S$_4$ are very similar to our observation on ZnGa$_2$Se$_4$. On the other hand, x-ray diffraction experiments for CdGa$_2$Se$_4$ show that the NaCl-type phase transforms into a zinc-blende-type structure below 5 GPa upon decompression and this structure is different to the defect-chalcopyrite structure. Our results are in good agreement with the studies of Marquina et al. and also they agree well with the conclusions drawn from Raman measurements on CdGa$_2$Se$_4$, CdGa$_2$S$_4$, ZnGa$_2$Se$_4$, and ZnGa$_2$S$_4$. In these studies the samples recovered at ambient pressure were found to be Raman inactive, while the zinc-blende structure is expected to have two Raman active phonons. In contrast with these results, Raman studies performed by Mitani et al. showed that Raman bands were recovered for CdGa$_2$Se$_4$ upon decompression, but they do not correspond to the defect-chalcopyrite structure. On top of that, unpublished optical-absorption measurements on single-crystalline CdGa$_2$Se$_4$ and ZnGa$_2$Se$_4$ show a new phase on pressure release from the high-pressure phase. In order to solve this puzzle, clearly more research is needed to clarify whether a metastable phase is obtained upon pressure release in digallium tetrathelenides and tetrathosphides or not.

C. Pressure dependence of the lattice parameters and equations of state

From the refinement of x-ray diffraction patterns we have obtained the pressure dependence of the lattice parameters for the low- and high-pressure phases. The pressure evolution of the structural parameters and the atomic volume ($V$) of ZnGa$_2$Se$_4$ and CdGa$_2$S$_4$ are shown in Figs. 4 and 5, respectively. To make it easier for comparison between the low- and high-pressure phases, we plotted $2V$ instead of $V$ for the NaCl-type phase. In ZnGa$_2$Se$_4$, the compression of the low-pressure phase is slightly anisotropic up to 10.4 GPa.
CdGa$_2$S$_4$, the compression of the low-pressure phase is constant within the uncertainty of the experiments. In MnGa$_2$Se$_4$ and CdGa$_2$Se$_4$, it also indicates that the collapse of about 5% is in agreement with the results reported for MnGa$_2$Se$_4$ and CdGa$_2$Se$_4$. For the low-pressure phase we obtained $V_0=333.08$ Å$^3$ (the measured value at ambient pressure outside the DAC), we obtained $B_0=47(2)$ GPa and $B'_0=3.9(3)$. For the NaCl-type structure of ZnGa$_2$Se$_4$, by fixing $V_0=156.5$ Å$^3$ (the measured value at ambient pressure in the recovered sample) and $B'_0=4$, we obtained $B_0=50(2)$ GPa. For the defect-chalcopyrite phase of CdGa$_2$S$_4$, by fixing $V_0=311.38$ Å$^3$ (the measured value at ambient pressure outside the DAC), we obtained $B_0=64(2)$ GPa and $B'_0=4.1(3)$. From these results we conclude that the low-pressure phase of ZnGa$_2$Se$_4$ has a similar compressibility to the low-pressure phases of MnGa$_2$Se$_4$, $B_0=44(2)$ GPa (Ref. 8) and CdGa$_2$Se$_4$. $B_0=42(2)$ GPa (Ref. 7) for the low-pressure phase. For the high-pressure phase of CdGa$_2$S$_4$ we do not have enough data points to determine its EOS parameters. However, apparently the cubic high-pressure phase is less compressible than the tetragonal phases, as we observed in ZnGa$_2$Se$_4$ and by Marquina et al. found in MnGa$_2$Se$_4$. We also conclude that the tetr sel enides are more compressible than the tetrasulphides, which is consistent with the fact that for binary compounds such as ZnSe, ZnS, CdSe, and CdS, the sulphides are harder than the selenides. $B_0=66$ GPa and $B'_0=47(2)$ GPa. Previously a bulk modulus of 66 GPa (88 GPa) was calculated for ZnGa$_2$Se$_4$ (CdGa$_2$S$_4$) using the equation deduced by Baranovskiy within a tight-binding approach. The same approach predicts a bulk modulus of 64 GPa for CdGa$_2$S$_4$. Our and previous measurements show that the tight-binding model overestimates $B_0$ by more than 40%.

The axial ratio $c/a$ increases from 1.988 at ambient pressure to 2 at 10.4 GPa and beyond this pressure the $c/a$ remains constant within the uncertainty of the experiments. In CdGa$_2$S$_4$, the compression of the low-pressure phase is highly anisotropic. In particular, $c/a$ increases from 1.835 to 1.913 from ambient pressure to 17 GPa following a nearly linear pressure dependence. The larger increase in the axial ratio in CdGa$_2$S$_4$ is related to the smaller compressibility of the $c$-axis in this compound. A similar behavior has been observed in MnGa$_2$Se$_4$ and CdGa$_2$Se$_4$; i.e., apparently the four sphalerite-derivative compounds become more symmetric prior to the occurrence of the phase transition. In ZnGa$_2$Se$_4$, the lattice parameters at 18.5 GPa are $a=5.064$ Å and $c=10.156$ Å for the low-pressure phase and $a=5.064$ Å for the high-pressure phase. Therefore, a volume collapse of about 4.6% is observed at the phase transition. In CdGa$_2$S$_4$, the lattice parameters at 17 GPa are $a=5.064$ Å and $c=10.156$ Å for the low-pressure phase, while for the high-pressure phase we obtained $a=4.911$ Å at 22 GPa, which implies a volume collapse of about 5%. The presence of the volume collapses is in agreement with the results reported for MnGa$_2$Se$_4$ and CdGa$_2$Se$_4$. It also indicates that the reported transition is a first-order transition.

The pressure-volume curves shown in Figs. 4 and 5 were analyzed using a Birch–Murnaghan EOS: $P=\frac{3}{2}B_0(x^{7/3}-x^{2/3})\times[1+\frac{4}{9}(B'_0-4)(x^{2/3}-1)]$, with $x=V_0/V$, where the parameters $V_0$, $B_0$, and $B'_0$ are the zero-pressure volume, bulk modulus, and pressure derivative of the bulk modulus, respectively. For the defect-stannite phase of ZnGa$_2$Se$_4$, by fixing $V_0=333.08$ Å$^3$ (the measured value at ambient pressure outside the DAC), we obtained $B_0=47(2)$ GPa and $B'_0=3.9(3)$. For the NaCl-type structure of ZnGa$_2$Se$_4$, by fixing $V_0=156.5$ Å$^3$ (the measured value at ambient pressure in the recovered sample) and $B'_0=4$, we obtained $B_0=50(2)$ GPa. For the defect-chalcopyrite phase of CdGa$_2$S$_4$, by fixing $V_0=311.38$ Å$^3$ (the measured value at ambient pressure outside the DAC), we obtained $B_0=64(2)$ GPa and $B'_0=4.1(3)$. From these results we conclude that the low-pressure phase of ZnGa$_2$Se$_4$ has a similar compressibility to the low-pressure phases of MnGa$_2$Se$_4$, $B_0=44(2)$ GPa (Ref. 8) and CdGa$_2$Se$_4$, $B_0=42(2)$ GPa (Ref. 7) for the low-pressure phase. For the high-pressure phase of CdGa$_2$S$_4$ we do not have enough data points to determine its EOS parameters. However, apparently the cubic high-pressure phase is less compressible than the tetragonal phases, as we observed in ZnGa$_2$Se$_4$ and by Marquina et al. found in MnGa$_2$Se$_4$. We also conclude that the tetr sel enides are more compressible than the tetrasulphides, which is consistent with the fact that for binary compounds such as ZnSe, ZnS, CdSe, and CdS, the sulphides are harder than the selenides. $B_0=66$ GPa and $B'_0=47(2)$ GPa. Previously a bulk modulus of 66 GPa (88 GPa) was calculated for ZnGa$_2$Se$_4$ (CdGa$_2$S$_4$) using the equation deduced by Baranovskiy within a tight-binding approach. The same approach predicts a bulk modulus of 64 GPa for CdGa$_2$S$_4$. Our and previous measurements show that the tight-binding model overestimates $B_0$ by more than 40%.
We also analyzed the pressure evolution of bond distances. From our Rietveld refinements we found that not only the structure of ZnGa$_2$Se$_4$ becomes more symmetric under compression but also the position of the Se atoms gradually approach the ideal position ($\frac{1}{4}, \frac{1}{4}, \frac{1}{8}$). In particular, the coordinate $x$ of Se change from 0.264 at ambient pressure to 0.257 at 13.3 GPa (the highest pressure were we observed a pure defect-stannite structure), while the $z$ coordinate of Se changes from 0.117 to 0.121. As a consequence of all these changes in the anion coordinates, the Ga–Se bond corresponding to the Ga atom located at the position 2$x$ is reduced 20% more than the other cation-Se bonds. Additionally, all the cation-Se bonds increase approximately 3%; and the Se–Se distances decrease 3% at the phase transition. The second change is caused by the volume collapse of the structure of ZnGa$_2$Se$_4$, while the first one is caused by the reordering of the cation positions. We also found that upon compression CdGa$_2$S$_4$ becomes more symmetric and that the position of the S atoms gradually approach the ideal position (1/4,1/4,1/8). In particular the $x$ coordinate of S changes from 0.270 at ambient pressure to 0.265 at 17 GPa and the $y$ coordinate of S changes from 0.260 to 0.250. On the other hand, the $z$ coordinate of S changes from 0.140 to 0.130. As a consequence of all these changes in the anion coordinates, the Cd–S bond is reduced around 50% more than the other cation-Se bonds. A similar preferred compressibility of the Cd–Se bonds has been reported in CdGa$_2$Se$_4$. Additionally, all the cation-S bonds increase approximately 8% and the S–S distances decrease 8% at the transition. As in ZnGa$_2$Se$_4$, the second change in CdGa$_2$S$_4$ is caused by a volume collapse and the first one by reordering of the cation positions.

It is interesting to see that in ZnGa$_2$Se$_4$ and CdGa$_2$Se$_4$ the Ga–Se bonds have a similar average compressibility. The same behavior can be deduced for MnGa$_2$Se$_4$ from the data reported in Ref. 8. Since in ternary compounds the bulk compressibility is related to the polyhedral compressibility it is not strange that the three studied digallium tetraseelenides have a similar compressibility. Therefore a bulk modulus close to 45 GPa should be expected also for HgGa$_2$Se$_4$.31

We mentioned above that an increase in the cationic disorder apparently takes place in ZnGa$_2$Se$_4$. This disorder may be the origin of the precursor effects of the transition observed in x-ray experiments in CdGa$_2$Se$_4$ (Ref. 7) and in Raman experiments in four different digallium tetraselenides and tetrathiphosphides.3 Optical-absorption measurements also detect the precursor effects on ZnGa$_2$Se$_4$ and CdGa$_2$Se$_4$ around 13 GPa, which are responsible of nonreversible changes in the optical-absorption edge.32 Earlier it was shown that an order-disorder phase transition takes place in defect-chalcopyrite tetraseelenides at high temperatures and ambient pressure only when the tetragonal distortion parameter $\delta=2-c/a$ is smaller than 0.05.32 A considerable reduction in this parameter was observed both in MnGa$_2$Se$_4$ and CdGa$_2$Se$_4$ before the transition to the rocksalt structure.7,8 In our case, we observed that this parameter decreases from 0.165 at ambient pressure to 0.087 at 17 GPa for CdGa$_2$Se$_4$. In ZnGa$_2$Se$_4$ $\delta$ is equal to 0.022 at ambient pressure and approaches zero before the phase transition. On top of that, we also found in both compounds a decrease in the anion distortion parameter $\sigma_0 = \sqrt{(x-0.25)^2+(y-0.25)^2+(z-0.125)^2}$ upon compression. This parameter decreases for ZnGa$_2$Se$_4$ from 0.0214 at ambient pressure to 0.0107 at 13.3 GPa and from 0.117 at ambient pressure to 0.052 at 17 GPa for CdGa$_2$Se$_4$. A similar decrease was also found upon compression for MnGa$_2$Se$_4$.8 According to Garbato et al.,19 both the reduction in $\delta$ and $\sigma_0$ causes an increase in the cation disorder. Thus, the relation suggested above is fully consistent with the Raman and diffraction peak broadening and the increase in the crystalline disorder observed during compression.

### D. Size criterion

According to an empirical rule (size criterion) proposed by Jayaraman et al.33 the transition pressure from tetrahedral to octahedral coordination in ABX$_4$ compounds (e.g., chalcopyrite CuGaSe$_2$) increases with decreasing the ratio between the averaged cation radius, $(r_A+r_B)/2$, and the anion radius, $r_X$. Other size criteria, similar to the rule of Jayaraman et al., have been proven to work satisfactorily to predict the transition pressure in ternary compounds.34,35 However, Beister et al.36 challenged the rule of Jayaraman et al. based upon data on LiInSe$_2$, CuInSe$_2$, and AgInSe$_2$. These authors proposed that the transition pressure should increase with the decreasing cation radius difference $|r_A-r_B|$. Other authors tried to rationalize the transition pressure from a fourfold-coordinated structure to a sixfold-coordinated structure using the crystal ionicity,3 but this approach did not give a clear systematic for the transition pressures of ABX$_2$ and AB$_2$X$_4$ compounds. By comparing all the data available in literature on 23 different tetragonal-coordinated ABX$_2$ and AB$_2$X$_4$ compounds, we will show that the transition pressure on these compounds can be rationalized using the ionic radius on cations and anions in a similar way than proposed by Jayaraman et al. Table III displays the transition pressures for 23 different ABX$_2$ and AB$_2$X$_4$ compounds with structures related to sphalerite and the ionic radii of the elements A, B, and X.37 Figure 6 shows the transition pressure as a function of $\xi=(r_A+r_B)/2r_X$. In the figure, it can be seen that most of the compounds of interest follows two clear systematics. One for those compounds is with large cations (1.35 $> r_A+r_B > 1.15$) and another for the compounds with small cations $(r_A+r_B < 1.15)$. It is interesting to see that also spinel-structured AB$_2$X$_4$ compounds seem to follow the same behavior. In particular, compounds such as ZnAl$_2$S$_4$, CuIr$_2$S$_4$, MgAl$_2$O$_4$, CuCr$_2$Zr$_2$S$_4$, and Zn$_2$TiO$_4$ match very well with the systematic reported in Fig. 6 (see Table III). As shown in Fig. 6, apparently also the compounds with 1.45 $> r_A+r_B > 1.35$ and 1.45 $> r_A+r_B$ have a similar tendency to the increase in the transition pressure with the increase in $\xi$. It is important to note here that the fitting lines shown in Fig. 6 for each cation-size regime are dependent on the high-pressure points. Unfortunately, in literature there are few data available for $\xi$ values from 0.35 to 0.4, which make the systematic proposed here only valid to make back-of-the-envelope estimations for transition pressures in compounds not yet studied upon compression. Regarding the rule proposed by Beister et al., it is clear from Table III that no possible correlation could be
TABLE III. Transition pressures and ionic radii of different sphalerite-related semiconductors. The factor $\xi = (r_A + r_B)/2r_X$ was calculated for each compound using the Shannon radii (Ref. 37).

| Compound          | Structure     | $r_A$ | $r_B$ | $r_X$ | $\xi$ | $|r_A - r_B|$ | $P_T$(GPa) | Reference |
|-------------------|---------------|-------|-------|-------|-------|--------------|------------|-----------|
| CuAlTe$_2$       | Chalcopyrite  | 0.60  | 0.39  | 2.21  | 0.2239| 0.21         | 8.3        | 44        |
| CuGaTe$_2$       | Chalcopyrite  | 0.60  | 0.47  | 2.21  | 0.2421| 0.13         | 9.4        | 45        |
| CuAlSe$_2$       | Chalcopyrite  | 0.60  | 0.39  | 1.98  | 0.2500| 0.21         | 13.2(1.2)  | 44 and 46 |
| ZnAl$_2$S$_4$    | Defect chalcopyrite | 0.60  | 0.39  | 1.84  | 0.2690| 0.21         | 14.4       | 47        |
| CuAl$_2$S$_4$    | Chalcopyrite  | 0.60  | 0.47  | 1.98  | 0.2702| 0.13         | 13.6(0.5)  | 3         |
| ZnGa$_2$Se$_4$   | Defect stannite | 0.60  | 0.47  | 1.98  | 0.2702| 0.13         | 16.5(2)    | 3 and 5   |
| ZnAl$_2$Ga$_4$S$_4$ | Chalcopyrite | 0.60  | 0.42  | 1.84  | 0.2771| 0.18         | 17         | 48        |
| CuGaSe$_2$       | Chalcopyrite  | 0.60  | 0.47  | 1.91  | 0.2801| 0.13         | 17(1)      | 49        |
| MnGa$_2$Se$_4$   | Defect chalcopyrite | 0.66  | 0.47  | 1.98  | 0.2854| 0.19         | 13(1)      | 8         |
| Cu$_2$S$_3$      | Chalcopyrite  | 0.6   | 0.47  | 1.84  | 0.2907| 0.13         | 16.5(0.5)  | 3         |
| ZnGa$_2$S$_4$    | Defect stannite | 0.60  | 0.47  | 1.84  | 0.2907| 0.13         | 21(1)      | 3         |
| ZnAl$_2$S$_2$    | Spinel        | 0.60  | 0.53  | 1.84  | 0.3070| 0.07         | 28         | 51, 52    |
| MgAl$_2$O$_4$    | Spinel        | 0.57  | 0.53  | 1.38  | 0.3985| 0.04         | 35(5)      |           |
| CuInTe$_2$       | Chalcopyrite  | 0.60  | 0.62  | 2.21  | 0.2692| 0.02         | 42(1.4)    | 45        |
| CdAl$_2$Se$_4$   | Defect chalcopyrite | 0.78  | 0.39  | 1.98  | 0.2955| 0.39         | 9.1(1)     | 47        |
| CuInSe$_2$       | Chalcopyrite  | 0.60  | 0.62  | 1.98  | 0.3081| 0.02         | 7.1        | 53        |
| CdGa$_2$Se$_4$   | Defect chalcopyrite | 0.78  | 0.47  | 1.98  | 0.3156| 0.31         | 16(1.5)    | 3, 6, 7    |
| CdAl$_2$S$_3$    | Defect chalcopyrite | 0.78  | 0.39  | 1.84  | 0.3179| 0.39         | 14(0.5)    | 47 and 54  |
| CuIn$_2$S$_3$    | Chalcopyrite  | 0.60  | 0.62  | 1.84  | 0.3315| 0.02         | 9.6        | 3         |
| CuIr$_2$S$_4$    | Spinel        | 0.57  | 0.68  | 1.84  | 0.3396| 0.11         | 13(1)      | 55        |
| CdGa$_2$S$_4$    | Defect chalcopyrite | 0.78  | 0.47  | 1.84  | 0.3396| 0.31         | 17(2)      | 3 and 4    |
| HgAl$_2$Se$_4$   | Defect chalcopyrite | 0.96  | 0.39  | 1.98  | 0.3409| 0.57         | 12.7       | 47        |
| AgGaS$_2$        | Chalcopyrite  | 0.79  | 0.47  | 1.84  | 0.3424| 0.32         | 15         | 3         |
| CuCrZrS$_4$      | Spinel        | 0.57  | 0.72  | 1.84  | 0.3505| 0.15         | 15         | 56        |
| Zn$_2$TiO$_4$    | Inverse spinel | 0.60  | 0.60  | 1.38  | 0.4347| 0            | 28(3)      | 57        |
| AgGaTe$_2$       | Chalcopyrite  | 0.98  | 0.47  | 2.21  | 0.3320| 0.51         | 5.4        | 58        |
| CdCr$_2$Se$_4$   | Spinel        | 0.78  | 0.62  | 1.98  | 0.3535| 0.16         | 9(1)       | 59        |
| AgGaSe$_2$       | Chalcopyrite  | 0.98  | 0.47  | 1.98  | 0.3661| 0.51         | 8.3        | 3         |
| MgIn$_2$S$_4$    | Spinel        | 0.57  | 0.80  | 1.84  | 0.3723| 0.23         | 10.5(1.5)  | 60        |
| MnIn$_2$S$_4$    | Spinel        | 0.66  | 0.80  | 1.84  | 0.3967| 0.14         | 8(1)       | 60        |
| CdIn$_2$S$_4$    | Spinel        | 0.78  | 0.80  | 1.84  | 0.4293| 0.02         | 11(1)      | 60        |

FIG. 6. Transition pressures of different $ABX_4$ and $AB_2X_3$ compounds as a function of $\xi = (r_A + r_B)/2r_X$. The solid lines estimate the transition pressure of different compounds, the dotted lines give the deviation from the estimated value. The data plotted correspond to those shown in Table III.

established between the transition pressures and cation radius difference $|r_A - r_B|$. We strongly believe that the comparison made by Beister et al. between LiInSe$_2$, CuInSe$_2$, and AgInSe$_2$ was inadequate and it also mislead these authors to challenge the rule of Jayaraman et al. LiInSe$_2$ has an orthorhombic structure ($Pna2_1$) that is not related to sphalerite and furthermore its cations do not have a tetrahedral coordination. Therefore, phenomenological comparisons are not possible between LiInSe$_2$ and the other two compounds. Further, the transition pressure for AgInSe$_2$ (2.5 GPa) was taken by Beister from resistivity and x-ray diffraction measurements performed under highly nonhydrostatic conditions.\(^{38}\) Uniaxial stresses are known to strongly affect pressure-induced phase transitions reducing the transition pressure by 10 GPa.\(^{13}\) On the other hand, selenides usually have higher transition pressures than isomorphous tellurides, and AgInTe$_2$ is known to remain stable at least up to 2.7 GPa according to x-ray diffraction experiments.\(^{39}\) So the early studies on AgInSe$_2$ are not good candidates to establish a systematic for $ABX_3$ compounds. From the systematic behavior of Fig. 6, a transition pressure of $8(2)$ GPa is predicted for AgInSe$_2$ ($r_A + r_B = 1.60$ and $\xi \approx 0.40$). This suggests that studies taking advantage of the state-of-the-art synchrotron facilities are needed to clarify the high-pressure structural behav-
ior of AgInSe₂. It would be also interesting to perform such studies on AgInS₂ and AgInTe₂. For these compounds we predict transition pressures of 12(2) and 4(2) GPa, respectively. In AgInS₂ and AgInTe₂ x-ray diffraction experiments have been performed only up to 5 GPa (Ref. 40) and 2.7 GPa, respectively, and the chalcopyrite structure found to be stable up to these pressures. An extension of these studies is required to test our predictions. The systematic proposed in this work could be also applied to other sphalerite-related compounds such as defect-chalcopyrite HgGa₂Se₄ (Ref. 31) and double-defective chalcopyrite In₃P₄S₆ (Ref. 42) for which transition pressures of 9(2) and 7(2) GPa are predicted. It is important to note here that the systematic established in this work cannot be applied to ABX₂ and AB₂X₄ compounds with structures not related to sphalerite similar to LiInSe₂, and like most of the alkaline-earth digallium tetraselenides, which usually crystallize in an orthorhombic structure. However, the same systematic apparently works well in spinel-structured AB₂X₄ compounds. At least in those the structural stability of the compound is not affected by Jahn–Teller effects caused by the presence of magnetic ions. One example of these compounds is MgAl₂O₄ (see Table III and Fig. 6). Based upon these facts, predictions can be made for the transition pressures of MgGa₂O₄ and MgIn₂O₄, for which transition pressures of 28(3) and 26(3) GPa are predicted. For the cases of ZnAl₂O₄ and CdAl₂O₄ we have predicted transition pressures as 37(4) and 33(4) GPa respectively.

To conclude the discussion, we would like to comment that in CuGaTe₂ and CuInTe₂ the following pressure-induced structural sequence is observed: chalcopyrite→rocksalt→Cmcn. The same structural sequence has been observed in sphalerite-structured binary semiconductors such as CdTe. Therefore, upon crystallochemical arguments it is quite reasonable to speculate the sphalerite related to NaCl-type transition for all the compounds reviewed here. Our results further suggest that at higher pressures a second transition to a Cmcn structure could take place in most of them.

IV. CONCLUSIONS

High-pressure ADXRD experiments on two sphalerite-related defective semiconductors have been reported. The results obtained show that ZnGa₂Se₄ has a tetragonal defect-stannite structure from atmospheric pressure to 15.2 GPa. Furthermore, the tetragonal structure coexists with a higher-symmetry cubic structure from 15.2 to 18.5 GPa, and beyond this pressure, only the cubic structure is stable up to 23 GPa. In CdGa₂Se₄ it has been found that the structure is a tetragonal defect chalcopyrite up to 17 GPa and beyond a pressure-induced phase transition takes place to a cubic structure similar to ZnGa₂Se₄. The results obtained were compared to those previously reported in isostructural compounds. The role played by cation disorder in the observed transition is discussed. Finally, a room temperature equation EOS for the title compounds is reported and a systematic for pressure-driven phase transitions in sphalerite-related compounds is discussed.

ACKNOWLEDGMENTS

This study was supported by the Spanish government MICINN under Grant Nos. MAT2007-65990-C03-01, MAT2006-02279, and CSD-2007-00045 and the Generalitat Valenciana (Project No. GV06/151). The U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences supported the use of the APS under Contract No. W-31-109-Eng-38. DOEBS, DOE-NNSA, NSF, DOD-TACOM, and the Keck Foundation supported the use of the HPCAT. D. Errandonea is indebted to the Fundación de las Artes y las Ciencias de Valencia for granting him the IDEA prize. F. J. Manjón acknowledges also financial support from “Vicerrectorado de Innovación y Desarrollo de la UPV” through Project No. UPV/2008-0020. Work at UNLV is supported by DOE Award No. DEFG36-05GO8502. The UNLV High Pressure Science and Engineering Center was supported by the DOENNSA under cooperative Agreement No. DE-FG52-06NA26274.

29. A. M. Pendás, A. Costales, M. A. Blanco, J. M. Recio, and V. Luana,
Errandonea et al.


