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High-pressure behaviour of selenium-based spinels and related structures—an experimental and theoretical study

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Abstract

The high-pressure structural behaviour of the cubic spinel CdCr_2Se_4 (space group $Fd\bar{3}m$) and tetragonal CdGa_2Se_4 ($I\bar{4}$) has been investigated experimentally and theoretically in order to understand the large difference in compressibility between the two selenides. The experimental values of the bulk modulus for these compounds are 101(2) and 48(2) GPa, respectively. These values compare well with 92 and 44 GPa obtained from first-principles calculations based on the density functional theory formalism. The observed difference in compressibility between the cubic and tetragonal structures can be understood in terms of polyhedral analysis. In a hypothetical cubic spinel structure ($Fd\bar{3}m$), the calculated bulk modulus for CdGa_2Se_4 is 85 GPa. This value together with the experimental and theoretical results for CdCr_2Se_4 suggest that the selenium-based cubic spinels should have a bulk modulus about 100 GPa, which is half the value found for the oxide spinels.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It has been observed that cubic spinel oxides, with chemical formula AB_2O_4 , respond in a similar way to hydrostatic pressure. In particular, the values of the bulk modulus for these

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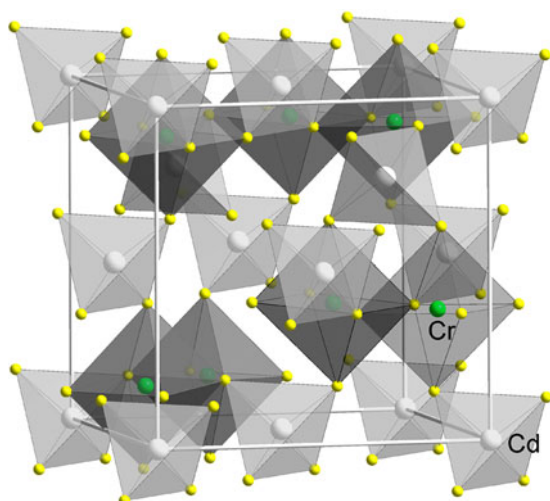


Figure 1. The tetrahedral and octahedral coordination of Cd^{2+} and Cr^{3+} ions in the cubic spinel CdCr_2Se_4 ($Fm\bar{3}m$).

compounds are confined within a narrow range around 200 GPa, e.g. 196 GPa for the prototype spinel MgAl_2O_4 [1], 206 GPa for NiMn_2O_4 [2], 197 GPa for ZnMn_2O_4 [3] and 198 GPa for CuMn_2O_4 [4]. This behaviour, originally suggested empirically by Finger *et al* [5], has recently been confirmed theoretically by Pendás *et al* [6] and Recio *et al* [7]. Essentially, the explanation is based on the fact that the oxygen anions form a nearly close-packed fcc structure, occupying most of the crystal volume. In this way, the overall compressibility is determined mainly by the oxygen sublattice.

In accordance with the arguments given above, it may be assumed that the values of the bulk modulus for selenium-based spinels and related structures are determined mainly by the selenium anions. In a previous work, we have investigated the effect of low temperature and high pressure on lattice distortions in $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$, where $x = 0.00, 0.06$ and 0.12 [8]. Pressure-induced phase transformations in CdGa_2Se_4 have recently been studied by Ursaki *et al* [9], Grzechnik *et al* [10] and Tiginyanu *et al* [11]. The present work is an experimental and theoretical investigation of the high-pressure behaviour of the end members of the $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$ system ($x = 0$ and 2), namely the selenium spinel CdCr_2Se_4 and cadmium gallium selenate CdGa_2Se_4 ; primarily, we are interested in the equation of state of these compounds, but we also give results for structural phase transformations at high pressure.

2. Experimental procedures

2.1. Sample preparation

CdCr_2Se_4 crystallizes at normal conditions in the cubic spinel structure, space group $Fd\bar{3}m$. The lattice constant at ambient conditions was determined in the present work as $a_0 = 10.743(6)$ Å, giving the unit-cell volume $V_0 = 1240(2)$ Å³. These values are in good agreement with data in the literature. CdCr_2Se_4 has a normal cation distribution where the Cd^{2+} ions are located at the tetrahedral interstitial sites of the selenium sublattice, and the Cr^{3+} ions are located at the octahedral sites (figure 1). Each unit cell contains eight formula units.

Single crystals of CdCr_2Se_4 were grown by vapour transport in a closed quartz ampoule containing CdSe and Ga_2Se_3 in solid form. Anhydrous CrCl_3 was used as the chemical

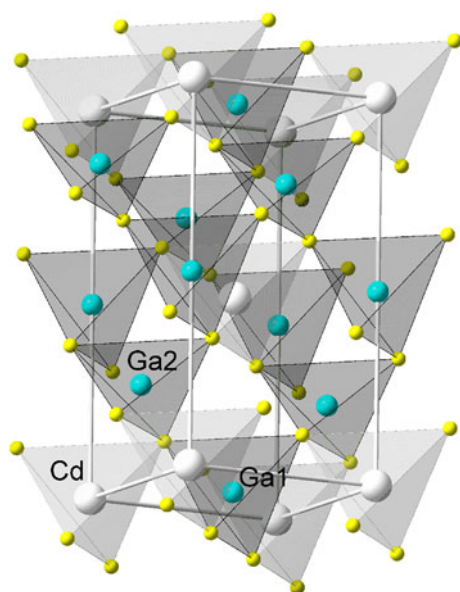


Figure 2. Crystal structure of CdGa_2Se_4 at ambient conditions ($I\bar{4}$).

transport agent. Details about the synthesis have been published elsewhere [12]. The resulting single crystals were of octahedral shape with regular $\{111\}$ faces, the edge length being 1–3 mm. For powder diffraction, the crystals were pulverized in an agate mortar.

Cadmium gallium selenate, CdGa_2Se_4 , crystallizes at normal conditions in a defect chalcopyrite structure, space group $I\bar{4}$, where one of the cation sites is vacant (figure 2). The unit cell, which contains two formula units, is tetragonal. The lattice constants at ambient conditions were determined in the present work as $a_0 = 5.753(5)$ Å and $c_0 = 10.745(10)$ Å, giving a c_0/a_0 ratio of 1.868(3), and unit-cell volume $V_0 = 355.6(8)$ Å³. These values are in good agreement with $a_0 = 5.743(2)$, $c_0 = 10.756(4)$ Å, $c_0/a_0 = 1.8729(10)$ and $V_0 = 354.8(3)$ Å³, measured by Krämer *et al* [13].

Powder samples of CdGa_2Se_4 were synthesized in vacuum-sealed quartz ampoules from high-purity elements Cd (0.508 g, 4.52 mmol), Ga (0.632 g, 9.06 mmol) and Se (1.43 g, 18.11 mmol). The ampoule with the reactants was evacuated and filled with nitrogen three times before sealing. Heating up to 1100 °C was carried out in various steps following the sequence published by Kshirsagar and Sinha [14]. The polycrystalline material was then removed and pulverized in an agate mortar. It was subsequently identified as pure CdGa_2Se_4 by powder x-ray diffraction.

2.2. High-pressure x-ray diffraction

Experimental single-crystal diffraction data were recorded by means of a Kuma Diffraction four-circle diffractometer (KM-4) equipped with a diamond-anvil high-pressure cell. Monochromatic x-rays of wavelength 0.71073 Å (Mo $K\alpha$ radiation) were used. The setting angles of 25 centred reflections in the range $10.7^\circ \leq 2\theta \leq 55^\circ$ were used for a least-squares fit of the unit-cell parameters without symmetry constraints. In particular, the unit-cell volume was determined as a function of pressure in order to describe the equation of state of the sample.

High-pressure powder x-ray diffraction patterns were recorded at room temperature using the white-beam method and synchrotron radiation at Station F3 of HASYLAB-DESY in

Hamburg, Germany. The diffractometer, working in the energy-dispersive mode, has been described elsewhere [15]. High pressures up to 40 GPa were obtained in a Syassen–Holzapfel-type diamond-anvil cell. A finely ground powder sample and a ruby chip were placed in a 200 μm diameter hole in the inconel gasket, preindented to a thickness of 60 μm . A 16:3:1 methanol:ethanol:water mixture was used as the pressure-transmitting medium. The pressure was determined by measuring the wavelength shift of the ruby R_1 and R_2 luminescence lines and applying the non-linear pressure scale of Mao *et al* [16]. The Bragg angle was calculated from a zero-pressure diffraction spectrum of NaCl in the diamond-anvil cell. The standard deviation of the pressure determination was about 0.1 GPa for pressures up to about 10 GPa. For higher pressure the e.s.d. might be larger because of possible non-hydrostatic conditions.

For each phase, the experimental pressure–volume data have been described by the Birch [17] or Murnaghan [18] equation of state:

$$P/B_0 = \frac{3}{2}(x^{-7/3} - x^{-5/3})\left[1 + \frac{3}{4}(B'_0 - 4)(x^{-2/3} - 1)\right] \quad (1a)$$

$$P/B_0 = (x^{-B'_0} - 1)/B'_0 \quad (1b)$$

where $x = V/V_0$, V is the volume at pressure P , V_0 is the volume at zero pressure, and B_0 and B'_0 are the isothermal bulk modulus and its pressure derivative, both parameters being evaluated at zero pressure. Values of B_0 and B'_0 are obtained from a least-squares fit of equation (1a) or (1b) to the experimental pressure–volume points. Usually, the two equations of state give practically the same result, but in some cases involving a narrow pressure range, we have encountered problems with our Birch-fitting program.

3. Computational aspects

First-principles calculations on CdGa_2Se_4 and CdCr_2Se_4 have been performed within the density functional theory formalism using the CRYSTAL [19] and ABINIT⁷ packages, respectively. For CdGa_2Se_4 , we have investigated the tetragonal $I\bar{4}$ phase, stable at ambient pressure, as well as a hypothetical cubic spinel structure. The latter was studied in both the normal $Fd\bar{3}m$ and the inverse $Im\bar{m}a$ disordered configuration. CRYSTAL calculations were carried out using the all-electron standard basis sets reported by Towler *et al* [20] and the exchange and correlation functionals involved in the so-called B3LYP approximation [21, 22]. At a number of selected volumes surrounding the experimental value, the total energy E of CdGa_2Se_4 has been minimized with respect to the unit-cell lattice parameters and the atomic coordinates of the selenium atom, (x, y, z) in the tetragonal structure and u in the cubic structure, by means of the Melder–Mead algorithm [23]. We have checked that the same optimized geometry is obtained if the Gibbs energy is used as the thermodynamic potential in the simulations of the crystal response to hydrostatic pressure.

In CdCr_2Se_4 , the ability of the ABINIT code to deal with open-shell systems has allowed us to obtain an accurate description of the low-temperature ferromagnetic character of its zero-pressure normal spinel structure [24, 25]. The ferromagnetic state is simulated by means of spin-polarized calculations that are performed by fixing the number of unpaired electrons according to the d^3 electronic configuration of Cr^{3+} . We have also explored the influence of the magnetic interactions on the elastic properties of CdCr_2Se_4 . To this end, (E, V) points are computed in a non-magnetic state with a closed-shell average electronic configuration, and compared with the results of the ferromagnetic calculation.

In both the calculations mentioned above, semi-core Hartwigsen–Goedecker–Hutter relativistic pseudopotentials have been used in the context of the local density approximation,

⁷ The ABINIT computer code is a collaborative project involving the Universit  Catholique de Louvain, Corning Incorporated, and other contributors (<http://www.abinit.org>).

using the Teter and Pade parametrization of the Ceperley–Alder exchange–correlation energy density [26]. Although the semi-core pseudopotentials imply high computational cost, they have proven necessary in order to obtain an accurate description of the electronic structure of the 3d ion. After convergence studies in the ferromagnetic and non-magnetic calculations, we have chosen a kinetic energy cut-off of 80 Hartree (40 Hartree) for the plane wave expansion, and a $2 \times 2 \times 2$ ($4 \times 4 \times 4$) Monkhorst–Pack [27] grid of special k -points for the Brillouin zone integration. The optimization of the internal coordinate u has been performed through the Broyden–Fletcher–Goldfarb–Shannon algorithm [28].

For each structure model considered, the volume response to hydrostatic pressure has been obtained by means of numerical methods and standard equations of state fitted to the corresponding set of computed (E, V) points. The resulting equation of state (EOS), $P(V)$, is then used to assign pressure values to the polyhedral volumes, into which the tetragonal and cubic unit cells can be decomposed. We refer to [29] and [30] for more details. For the tetragonal phase, the cationic polyhedra are CdSe_4 and two types of GaSe_4 tetrahedra, whereas in the cubic phases the cationic polyhedra are CdSe_4 and CrSe_6 (in CdCr_2Se_4), CdSe_4 and GaSe_6 (in the normal CdGa_2Se_4 spinel), and GaSe_4 , CdSe_6 and GaSe_6 (in the inverse CdGa_2Se_4 spinel). This simple polyhedral partition is used here to analyse differences and similarities among the macroscopic compressibilities observed experimentally for the CdGa_2Se_4 and CdCr_2Se_4 polymorphs.

4. Results and discussion

4.1. Experimental results

High-pressure powder x-ray diffraction has shown that CdCr_2Se_4 ($Fd\bar{3}m$) undergoes a structural pressure-induced phase transformation at about 10 GPa, and that the diffraction patterns of the high-pressure phase can be indexed according to a tetragonal distortion of the cubic unit cell [8]. Here we give experimental compressibility data for the cubic spinel phase of CdCr_2Se_4 , obtained by single-crystal diffraction for pressures less than 5 GPa (table 1). A fit of the Murnaghan equation (1b) to these data results in $B_0 = 101.2(23)$ GPa and $B'_0 = 5.2(14)$, where the uncertainties are the standard errors of the least-squares fit.

The pressure-induced phase transitions in CdGa_2Se_4 have recently been investigated by Ursaki *et al* [9] and Grzechnik *et al* [10]. In the latter reference it is shown that there is an order–disorder phase transition to the rocksalt structure, space group $Fm\bar{3}m$, at about 21 GPa. The cubic unit cell contains one formula unit. The Se atoms are located at the 4b site, while the Cd and Ga atoms are located at the 4a site with occupancy factors 0.25 and 0.5, respectively. Typical diffraction patterns from our work are shown in figure 3. The transition pressure, P_c , has been determined by plotting the ratio between the observed peak heights (corrected for background) of the 200 reflection of the high-pressure phase and the 112 reflection of the low-pressure phase as shown in figure 4. The transition pressure $P_c = 21.7$ GPa is defined by extrapolating the steep part of the curve to zero intensity of the 200 reflection. The value of the transition pressure is in very good agreement with 21.4 GPa as quoted by Grzechnik *et al* [10]. Figures 5 and 6 show the pressure dependence of the lattice parameters of the two phases, and the c/a ratio of the tetragonal phase, respectively. Included in the figures are the numerical data points given by Grzechnik *et al* [10], showing good agreement. The volume collapse at the phase transition is found to be 6%, also in good agreement with Grzechnik *et al* [10].

In table 2 we present our experimental compressibility data for the defect chalcopyrite structure of CdGa_2Se_4 , obtained by powder diffraction, for pressures of less than 10 GPa. A least-squares fit of the Birch equation (1a) to these data gives $B_0 = 48.3(20)$ GPa and $B'_0 = 4.8(4)$. Grzechnik *et al* [10] quote the corresponding values 41.5(2) GPa and 5.0(10).

Table 1. Compressibility data for cubic CdCr₂Se₄ ($Fd\bar{3}m$). V is the unit-cell volume at pressure P , and V_0 is the corresponding zero-pressure volume. The experimental data have been obtained by high-pressure single-crystal diffraction. The theoretical data have been calculated for (a) the non-magnetic state and (b) the ferromagnetic state.

P (GPa)	$(V/V_0)_{\text{expt}}$	$(V/V_0)_{\text{theor (a)}}$	$(V/V_0)_{\text{theor (b)}}$
0.00	1.0000(15)	1.0000	1.0000
0.65	0.9935(15)	0.9931	0.9921
0.80	0.9929(15)	0.9915	0.9902
1.22	0.9888(15)	0.9872	0.9852
1.40	0.9874(15)	0.9854	0.9837
1.65	0.9846(15)	0.9829	0.9810
1.95	0.9816(15)	0.9800	0.9777
2.15	0.9795(15)	0.9780	0.9756
2.45	0.9769(15)	0.9751	0.9724
2.75	0.9747(15)	0.9722	0.9693
2.85	0.9734(16)	0.9713	0.9683
3.30	0.9704(16)	0.9669	0.9638
4.05	0.9647(17)	0.9609	0.9564
4.60	0.9598(17)	0.9562	0.9510

The 15% difference in B_0 is outside the estimated uncertainty of 5% in the present work, suggesting a systematic error. The reason for this discrepancy is not clear to us, but an explanation might be the influence of possible non-hydrostatic conditions. As can be seen in figures 5 and 6, the scatter of the present data increases at pressures above about 8 GPa. The reproducibility of our data has been checked by repeated experimental runs at the synchrotron radiation source. It may be noted in passing that the calculated bulk modulus, as will be shown below, is close to the mean value of the two experimental results. Besides, the discrepancy does not have any influence on the conclusion that the value of the bulk modulus for the tetragonal phase is about half the value for a hypothetical cubic spinel phase with the same composition (section 4.2).

Grzechnik *et al* [10], using angle-dispersive diffraction, carried out a detailed analysis of the pressure dependence of the structural parameters of CdGa₂Se₄, including the Ga(1)–Se–Ga(2) and Cd–Se–Ga(1) inter-tetrahedral angles as well as the angles in the CdSe₄ and Ga(2)Se₄ tetrahedra, and we refer to their paper.

4.2. Theoretical results

The calculated zero-pressure equilibrium properties of the ferromagnetic ($a = 10.574 \text{ \AA}$, $u = 0.2653$, $B_0 = 80.2 \text{ GPa}$, $B'_0 = 5.85$) and non-magnetic ($a = 10.375 \text{ \AA}$, $u = 0.2664$, $B_0 = 92.0 \text{ GPa}$, $B'_0 = 4.59$) states of the normal CdCr₂Se₄ spinel reveal a slight influence from the magnetic interactions on the unit cell and EOS parameters. The comparison with experimental data at room temperature, where CdCr₂Se₄ behaves as a paramagnetic solid, shows differences of 3% for the lattice parameter and 10% for B_0 . The agreement between theory and experiment is considered satisfactory. This is also illustrated by the theoretical P versus V/V_0 data in the experimental pressure range, as given in table 1. All these results have been obtained using the ABINIT code.

Similar agreement with experimental data is found for the corresponding zero-pressure properties of tetragonal CdGa₂Se₄ as calculated with the CRYSTAL package. The computed values for the lattice constants a_0 and c_0 are 5.990 and 10.687 \AA , and show deviations with

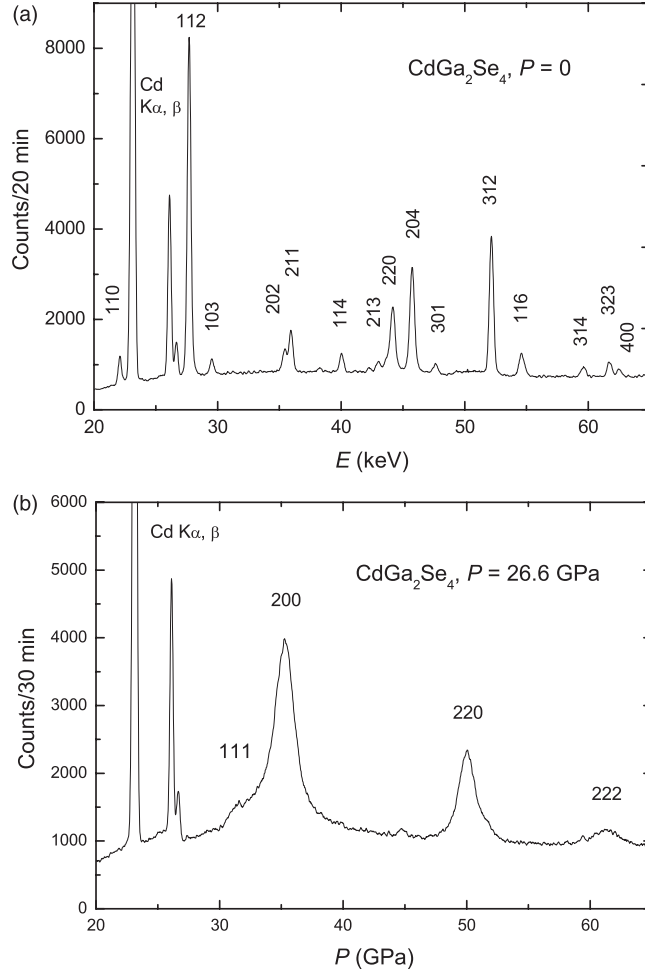


Figure 3. Energy-dispersive diffraction patterns of CdGa_2Se_4 . (a) Defect chalcopyrite ($I\bar{4}$) structure at ambient pressure. (b) Rocksalt ($Fm\bar{3}m$) structure at 26.6 GPa. Bragg angle $\theta = 3.96^\circ$.

respect to the experimental data of 4% and 1%, respectively. The corresponding c_0/a_0 ratio of 1.784 is 4.6% lower than the experimental value. For the bulk modulus, our calculations give $B_0 = 44.3$ GPa, i.e. a value in between the present experimental result and that given by Grzechnik *et al* [10]. For the pressure derivative, we get $B'_0 = 3.38$ in reasonably good agreement with experiment.

The deviations are within the expectations of the B3LYP strategy that tends to overestimate the unit-cell volume and underestimate the bulk modulus [27]. It is concluded that the theoretical results support the experimental EOS parameters obtained in the present work (cf also the calculated $P-V/V_0$ data in table 2). In particular, theory has confirmed the large difference in bulk modulus between cubic CdCr_2Se_4 (B_0 around 100 GPa) and tetragonal CdGa_2Se_4 (B_0 around 50 GPa).

It is also interesting to explore the high-pressure behaviour of CdGa_2Se_4 in a hypothetical cubic spinel structure. Our predictions are $B_0 = 84.8$ GPa and $B'_0 = 4.71$ for the normal spinel, and $B_0 = 85.1$ GPa and $B'_0 = 4.74$ for the inverse spinel. These values are reasonably

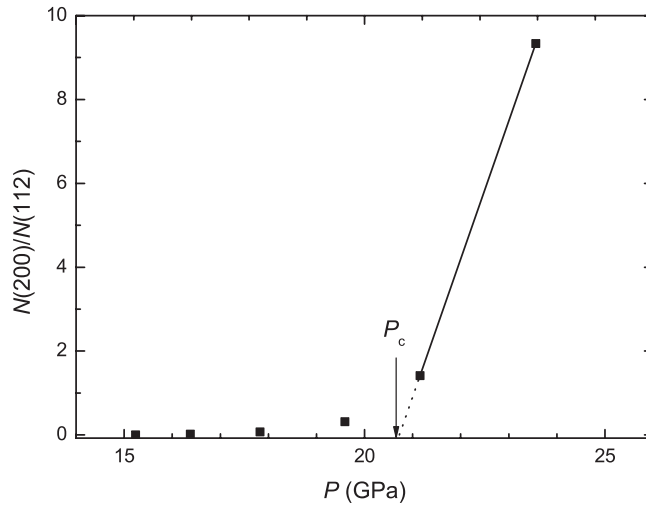


Figure 4. Pressure dependence of the ratio between the observed intensities of the 200 peak of the rocksalt ($Fm\bar{3}m$) structure and the 112 peak of the defect chalcopyrite ($I\bar{4}$) structure of CdGa_2Se_4 . N is the number of counts at the peak height (corrected for background) in a given time. P_c = transition pressure.

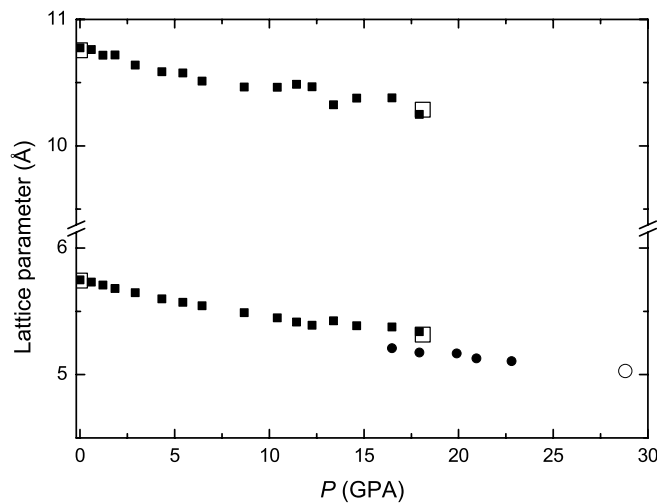


Figure 5. Pressure dependence of the lattice parameters of CdGa_2Se_4 in the tetragonal defect chalcopyrite ($I\bar{4}$) structure (squares), and the cubic rocksalt ($Fm\bar{3}m$) structure (circles), respectively. Experimental results of the present work are denoted by filled symbols, the results of Grzechnik *et al* [10] by open symbols.

close to the corresponding values for the CdCr_2Se_4 spinel. Therefore it can be concluded that the packing efficiency, rather than the nature of the constituent ions, is crucial for the large difference in compressibility between cubic and tetragonal selenium-based structures.

To analyse these similarities and differences further, we make use of the elementary cationic polyhedra [30, 31]. In the normal CdGa_2Se_4 and CdCr_2Se_4 spinels, the volume of their respective CdSe_4 tetrahedra is about the same, whereas the volume of CrSe_6 is slightly lower than GaSe_6 due to the greater size of Ga^{3+} compared with that of Cr^{3+} . The positive slope

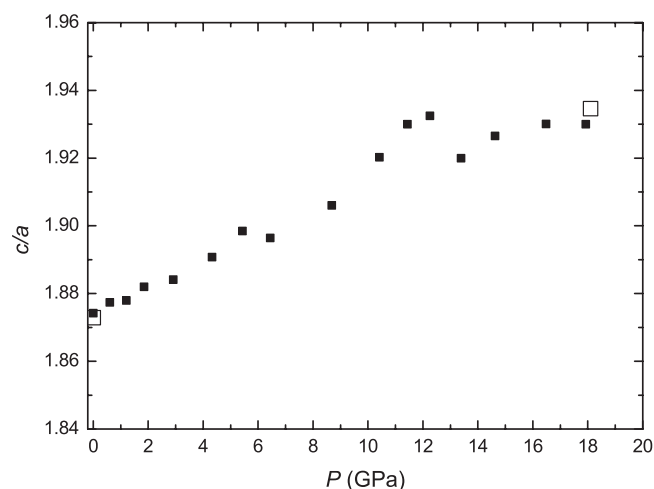


Figure 6. The c/a ratio for CdGa_2Se_4 in the tetragonal defect chalcopyrite ($I\bar{4}$) structure. The notation is as for figure 5.

Table 2. Compressibility data for the defect chalcopyrite structure of CdGa_2Se_4 ($I\bar{4}$). V is the unit-cell volume at pressure P , and V_0 is the corresponding zero-pressure volume. The experimental data have been obtained by high-pressure powder diffraction.

P (GPa)	$(V/V_0)_{\text{expt}}$	$(V/V_0)_{\text{theor}}$
0.00	1.0000(20)	1.0000
0.30	0.9930(20)	0.9933
0.60	0.9887(20)	0.9868
0.60	0.9876(20)	0.9868
1.30	0.9760(20)	0.9724
1.34	0.9752(20)	0.9716
1.80	0.9672(20)	0.9626
1.84	0.9665(20)	0.9618
2.60	0.9532(20)	0.9478
2.91	0.9478(20)	0.9423
3.21	0.9411(20)	0.9371
4.47	0.9271(20)	0.9165
4.52	0.9264(20)	0.9157
5.25	0.9171(30)	0.9048
5.24	0.9169(30)	0.9047
6.34	0.9025(30)	0.8890
6.44	0.9012(30)	0.8877
7.12	0.8942(30)	0.8784
8.28	0.8811(30)	0.8636
8.30	0.8809(30)	0.8633
8.65	0.8772(30)	0.8590
9.74	0.8661(30)	0.8461

of the u versus P curve suggests the inverse configuration for the CdGa_2Se_4 spinel. In fact, this disordered configuration is found to be lower in energy. Our simulation gives polyhedral bulk moduli around 100 and 70 GPa for the octahedra and tetrahedra, respectively, in both the normal CdCr_2Se_4 spinel and the inverse CdGa_2Se_4 spinel. It should therefore be noted that

the macroscopic B_0 value can be obtained by averaging the octahedral and tetrahedral bulk moduli. Furthermore, if we analyse the bond compressibilities in the normal spinels we find the expected behaviour with Cd–Se bonds more compressible than with Ga–Se and Cr–Se bonds, which exhibit similar bond length reductions under pressure.

The results, reported above, indicate that, in analogy with the oxide spinels [28], the selenium-based spinels also should exhibit a uniform response to hydrostatic pressure. The selenium compounds have a higher compressibility (lower bulk modulus) than their oxide counterparts, mainly due to the greater size and greater polarizable character of the Se^{2-} anion as compared with the O^{2-} anion. Extrapolating from the present theoretical and experimental results, one may predict that the bulk modulus of all cubic selenium spinels should be about 100 GPa, which is about half the value found for the oxide spinels. It should be noted that selenide spinels have molecular volumes around twice as large than oxide spinels in accordance with the empirical B – V inverse law.

Also the observed difference in compressibility between the tetragonal and cubic selenium-based structures can be understood in terms of polyhedral analysis. In the tetragonal phase, CdSe_4 and GaSe_4 tetrahedra fill less than 15% of the unit-cell volume, whereas in the spinel structure (normal or inverse configurations) the fractional occupancy of the cationic polyhedra is larger than 30%. This is due to the existence of six-fold coordination in the cubic structure, since the tetrahedra occupy similar volumes in both phases. Moreover, the presence of octahedra in the spinel structure produces a greater density of cation–anion bonds in the cubic structure than in the tetragonal structure. Thus, the increase of the cation coordination is, as expected, crucial for the greater resistance of the spinel structure ($Fd\bar{3}m$) to compression as compared with the tetragonal structure ($I\bar{4}$).

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