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Abstract
The vibrational spectra of $CdGa_2S_4$ and $CdGa_2Se_4$ under pressure were calculated with an *ab initio* technique and compared to the experimental results of Ursaki *et al* (Ursaki V V, Burlakov I I, Tiginyanu I M, Raptis Y S, Anastassakis E and Anedda A 1999 *Phys. Rev.* B **59** 257). The comparison is good even though the conclusions are different. Ursaki *et al* concluded that $CdGa_2S_4$ and $CdGa_2Se_4$ are disordered under pressure while here these materials remained ordered. The pressure dependence of the band gap is calculated to help clarify whether or not the disordering is occurring.

1. Introduction

$CdGa_2S_4$ and $CdGa_2Se_4$ are *ordered-vacancy* compounds, which means they can be described as tetrahedrally bonded frameworks if one assumes that their structures contain ordered arrays of vacancies [2, 3]. Many ordered-vacancy compounds do not show crystallographic ordering at room temperature and it is believed that this is due to the vacancies which cause order–disorder transitions. Bernard and Zunger [4] proposed that the disordering mechanism in ordered-vacancy compounds occurs in two stages and that the vacancies participate in the second stage. Recently, Ursaki *et al* [1] have measured the vibrational spectra under pressure of AGa_2X_4 (A = Cd, Zn; X = S, Se) and found that these materials disorder with the application of pressure as proposed in [4].

The ordered-vacancy compounds $A^{II}B_2^{III}C_4^{VI}$ are materials that are interesting as regards industrial applications, such as in non-linear optics and photovoltaics [5–7]. In spite of this interest, there has not been much *ab initio* research on them. It is hoped that the *ab initio* results in this paper will contribute to the understanding of the vibrational and electronic properties of ordered-vacancy compounds under pressure.

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2. Method and results

CdGa$_2$S$_4$ and CdGa$_2$Se$_2$ crystallize in the $I\bar{4}$ structure. This structure was relaxed using an *ab initio* method combined with the conjugate gradient technique allowing for variations in the shape of the cell and in the atomic positions [8]. The *ab initio* method is based on the local-density approximation (LDA) for the density functional theory with ultrasoft Vanderbilt-type pseudopotentials [9, 10]. The LDA used is of the Ceperley–Alder form [11] as parametrized by Perdew and Zunger [12]. The integration over the Brillouin zone was carried out using the Monkhorst–Pack scheme [13] and the eigenstates were expanded in plane waves. The simulation was converged using an energy cut-off of 15.70 Ryd and 12 k-points.

The curve for the energy versus volume was obtained after relaxing several volumes and it was fitted to the Birch–Murnaghan equation of state[2]. From this fitting one extracts both structural information and the pressure–volume relation. Figure 1 shows the Birch–Murnaghan curve and table 1 contains the values of the parameters in the Birch–Murnaghan equation.
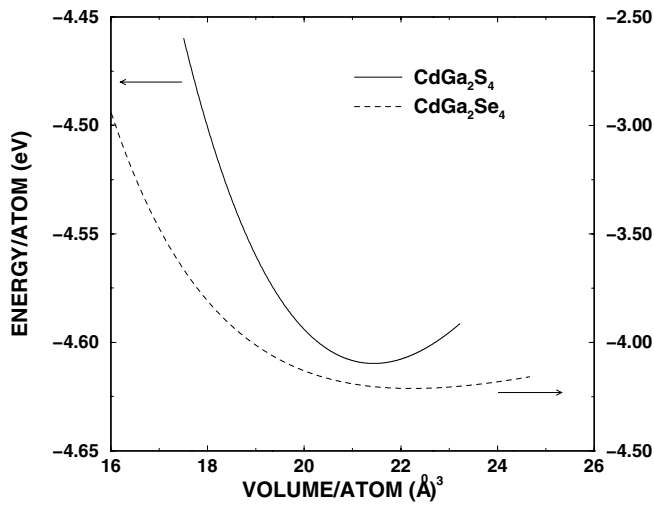
Figure 1. Equations of state of CdGa$_2$S$_4$ and CdGa$_2$Se$_4$. The left and right axes represent the energy per atom of CdGa$_2$S$_4$ and CdGa$_2$Se$_4$, respectively (as shown by ← and → in the plot).

Table 1. The parameters of the Birch–Murnaghan equations of state of CdGa$_2$S$_4$ and CdGa$_2$Se$_4$. These parameters are the minimum energy E_0, the equilibrium volume V_0, the bulk modulus K, and the pressure derivative of the bulk modulus K'.

Compound	E_0 (eV/atom)	V_0 (volume/atom)	K (GPa)	K'
CdGa$_2$S$_4$	−4.61	21.46	46.0	4.50
CdGa$_2$Se$_4$	−4.21	24.4	41.0	5.42

The positions of the atoms, in fractional coordinates, in the $I\bar{4}$ structure are as follows: Cd is at 2a, $(0, 0, 0)$; Ga1 at 2b, $(0, 0, \frac{1}{2})$; Ga2 at 2c, $(0, \frac{1}{2}, \frac{1}{4})$; and S or Se at 8g, (x, y, z). In the experiment of Hahn *et al* [15], the position of S is $(0.27, 0.26, 0.14)$ and the position of Se is

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[2] The equation is

$$E(V) = E_0 + \frac{9}{8}KV_0((V_0/V)^{2/3} - 1)^2\left(1 + \left(\frac{4 - K'}{2}\right)\left(1 - \left(\frac{V_0}{V}\right)^{2/3}\right)\right).$$

See reference [14].

(0.25, 0.26, 0.13); the values found here are (0.273, 0.265, 0.138) and (0.278, 0.254, 0.141) for S and Se, respectively.

Since $I\bar{4}$ is tetragonal, the shape of its conventional cell is given by the cell sides a and c. The experimental [15] a and c are ($a = 5.56$ Å, $c = 10.00$ Å) for CdGa$_2$S$_4$ and ($a = 5.73$ Å, $c = 10.70$ Å) for CdGa$_2$Se$_4$. The theoretical values are: ($a = 5.47$ Å, $c = 10.04$ Å) and ($a = 5.65$ Å, $c = 10.7$ Å) for CdGa$_2$S$_4$ and CdGa$_2$Se$_4$, respectively.

The vibrational spectra at different pressures were calculated at the Γ point with the same method as was used in [16, 17]. One begins with the equilibrium structure at a certain pressure and produces a distortion by displacing a *single* atom by a small amount U_0. The atomic forces resulting from the distortion are computed and the ratio of these forces and the corresponding displacement U_0 give one complete row of the $\vec{k} = \vec{0}$ force-constant matrix. Symmetry operations applied to these rows produce the entire force-constant matrix. Within the harmonic approximation the method is exact and anharmonic terms are avoided by averaging the calculations with displacements $+U_0$ and $-U_0$. The displacements U_0 had a value of 0.2 Å and were in the directions $\vec{x}$, $\vec{y}$, and $\vec{z}$, for Ga1, Ga2, and S (Se), and $\vec{x}$, $\vec{z}$ for Cd.

The $I\bar{4}$ phase contains seven atoms per unit cell and there are $(3 \times 7) - 3 = 18$ optical zone-centre modes. The vibrational modes comprise $3A + 5B + 5E$ representations [18], all of which are Raman active with the E and B modes infrared active as well; the E mode is doubly degenerate. The *ab initio* dependence with pressure of the vibrational spectra is shown in figure 2(a) for CdGa$_2$S$_4$ and in figure 3(a) for CdGa$_2$Se$_4$; the experimental results [1] are reproduced in figure 2(b) and figure 3(b). Experimental and theoretical results were fitted to the polynomial $\omega = \omega_0 + aP + bP^2$. The values of ω_0, a, and b are shown in table 2 for CdGa$_2$S$_4$ and in table 3 for CdGa$_2$Se$_4$.
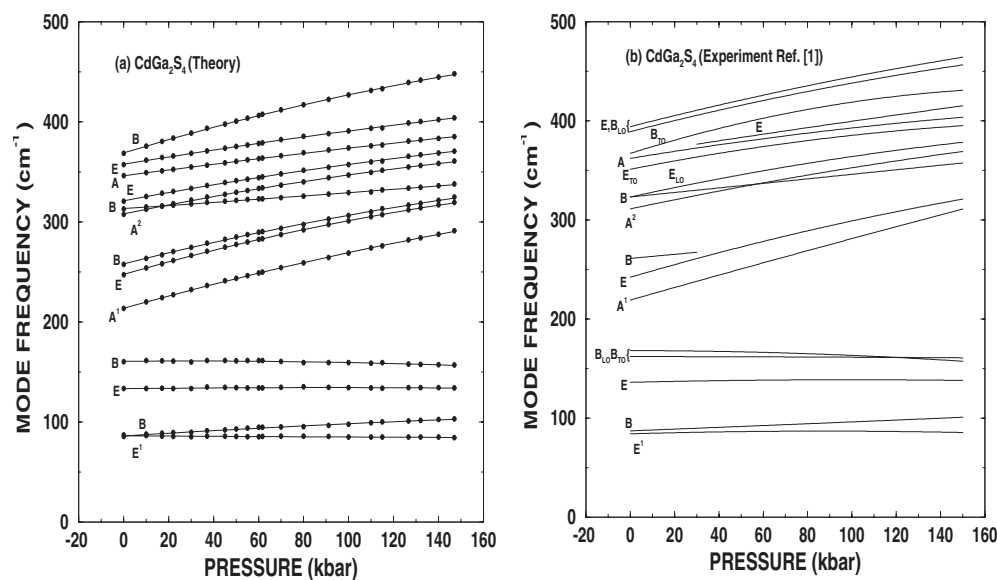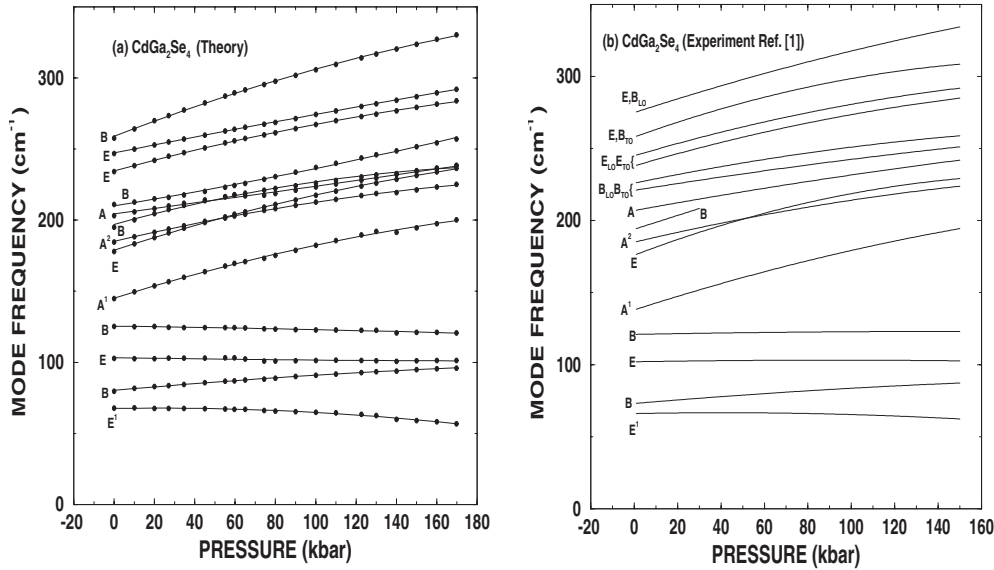

Figure 2. Comparison between the theoretical and experimental vibrational spectra under pressure of CdGa$_2$S$_4$. (a) Theoretical results; (b) experimental results. The symmetry of each mode is written beside the corresponding curve.

Figures 2(a), 2(b) and 3(a), 3(b) show good agreement between theory and experiment. This is further quantified in tables 2 and 3, where one can see that theory and experiment agree as regards (i) the symmetry assignment of the modes, (ii) the vibrational spectra at zero

Table 2. The dependence on pressure of the vibrational spectra at $\vec{k} = \vec{0}$ of CdGa$_2$S$_4$. The theoretical and experimental results of reference [1] (shown in brackets) were fitted to the polynomial $\omega = \omega_0 + aP + bP^2$. The modes E^1, A^1, and A^2 have been labelled with superscripts for easy comparison with experimental results.

Curve	Symmetry	ω_0 (cm^{-1})	a (10^{-1} cm^{-1} kbar^{-1})	b (-10^{-4} cm^{-1} kbar^{-2})
1	E^1 (E$^1_{LO,TO}$)	86.12 (84)	-0.16 (0.63)	0.35 (3.62)
2	B (B$_{LO,TO}$)	86 (87)	1.3 (0.88)	1.2 (-0.22)
3	E (E$_{LO,TO}$)	133.1 (136)	0.26 (0.52)	1.6 (2.63)
4	B (B$_{LO,TO}$)	160.45 (162, 168)	0.22 (-0.03, -0.02)	3.4 (0.38, 4.65)
5	A^1 (A^1)	213.63 (219)	6.2 (6.36)	7.0 (1.62)
6	E (E$_{LO,TO}$)	247.5 (242)	6.4 (6.54)	10.5 (8.55)
7	B (B$_{LO,TO}$)	257.82 (261)	5.7 (2.07)	8.4 (—)
8	A^2 (A^2)	307.89 (311)	4.6 (4.72)	7.4 (5.73)
9	B (B$_{LO,TO}$)	313.16 (323)	1.5 (2.29)	0.73 (—)
10	E (E$_{LO,TO}$)	321 (323, 351)	4.2 (4.89, 4.40)	6.0 (8.07, 9.80)
11	A (A)	346 (362)	3.0 (3.66)	2.1 (5.96)
12	E (E, B$_{TO}$)	357.5 (366, 367)	3.7 (3.49, 7.02)	4.0 (1.48, 18.5)
13	B (E, B$_{LO}$)	368.9 (389, 394)	6.8 (5.71, 5.71)	10.1 (8.16, 6.93)

Figure 3. Comparison between the theoretical and experimental vibrational spectra under pressure of CdGa$_2$Se$_4$. (a) Theoretical results; (b) experimental results. The symmetry of each mode is written beside the corresponding curve.

pressure, and (to a lesser extent) (iii) in the pressure dependence of the vibrational spectra. The discrepancy in ω_0, which gives the vibrational spectra at zero pressure, is less than 7%. The values of the constants a and b for the modes 1, 2, and 4 of CdGa$_2$S$_4$ are not in good agreement with the experiment. The same is true for the modes 3, 4, 9, and 10 of CdGa$_2$Se$_4$.

Ursaki *et al* [1] concluded that CdGa$_2$S$_4$ and CdGa$_2$Se$_4$ disorder under exposure to pressure in two consecutive stages as proposed by Bernard and Zunger [4]. The first stage

Table 3. The dependence on pressure of the vibrational spectra at $\vec{k} = \vec{0}$ of CdGa$_2$Se$_4$. The theoretical and experimental results of reference [1] (shown in brackets) were fitted to the polynomial $\omega = \omega_0 + aP + bP^2$. The modes E^1, A^1, and A^2 have been labelled with superscripts for easy comparison with experimental results.

Curve	Symmetry	ω_0 (cm^{-1})	a (10^{-1} cm^{-1} kbar^{-1})	b (-10^{-4} cm^{-1} kbar^{-2})
1	E^1 (E$^1_{LO,TO}$)	67.54 (66)	0.22 (0.30)	5.0 (3.66)
2	B (B$_{LO,TO}$)	80.23 (73)	1.26 (1.28)	2.0 (2.21)
3	E (E$_{LO,TO}$)	103.30 (102)	−0.22 (0.24)	−0.55 (1.32)
4	B (B$_{LO,TO}$)	125.4 (121)	−0.17 (0.28)	0.65 (0.95)
5	A^1 (A^1)	145.15 (138)	4.45 (4.85)	7.27 (7.23)
6	E (E$_{LO,TO}$)	178.83 (176)	4.64 (5.73)	7.50 (14.56)
7	A^2 (A^2)	185.05 (185)	3.37 (3.56)	6.1 (6.45)
8	B (B$_{LO,TO}$)	197.03 (194)	3.93 (4.81)	9.3 (—)
9	A (A)	204.52 (207)	1.9 (2.74)	−0.46 (2.71)
10	B (B$_{LO,TO}$)	210.02 (221, 226)	2.35 (2.43, 3.12)	−2.81 (2.76, 6.17)
11	E (E$_{LO,TO}$)	234.7 (238, 245)	3.85 (4.41, 4.45)	5.76 (8.50, 8.78)
12	E (E, B$_{TO}$)	247.4 (258)	2.82 (5.44)	1.14 (13.77)
13	B (E, B$_{LO}$)	259.0 (275)	5.52 (4.90)	7.89 (6.23)

is $I\bar{4} \rightarrow I\bar{4}2m$(disordered) and takes place when the cations Cd and Ga substitute for one another. The second stage is $I\bar{4}2m$(disordered) $\rightarrow P\bar{4}2m$(disordered) and takes place when the vacancies and the cations substitute for one another. Ursaki *et al* [1] found that at 55 kbar for CdGa$_2$S$_4$ and at 80 kbar for CdGa$_2$Se$_4$, the intensity peak of one A mode (denoted as A^1 in tables 2 and 3) started to decrease and to broaden. Since the $I\bar{4}2m$ phase has one less A mode than the $I\bar{4}$ phase, they concluded that the changes in A^1 were due to the first stage of disordering. To support this conclusion they noted that the frequency of the lowest E mode (E^1) decreases with pressure, starting this decreasing at 40 kbar in CdGa$_2$S$_4$ and at 85 kbar in CdGa$_2$Se$_4$. The second stage of disordering was found at 100 kbar for CdGa$_2$S$_4$ and at 110 kbar for CdGa$_2$Se$_4$, where the intensity peak of the A^2 mode started to decrease and to broaden. The theoretical and experimental dependences on pressure of the modes E^1, A^1, and A^2 are shown in figures 4(a), 4(b) for CdGa$_2$S$_4$ and CdGa$_2$Se$_4$, respectively. It is seen that theory and experiment are in good agreement and that theory finds that the E^1 mode decreases from 0 kbar in CdGa$_2$S$_4$ and from 80 kbar in CdGa$_2$Se$_4$.

Figure 5 shows the dependence on pressure of the band gap of CdGa$_2$S$_4$ and CdGa$_2$Se$_4$. The band gap of CdGa$_2$S$_4$ is not a smooth function of pressure. The band gap increases within the intervals 0 to 61 kbar and 91 to 108 kbar, and decreases within the intervals 61 to 91 kbar and 108 to 147 kbar. Further research revealed that the odd behaviour of the band gap between 61 and 108 kbar is not due to crossing of different bands at the top of the valence band. At 108 kbar, the band gap of CdGa$_2$S$_4$ is maximum with a value of 2.34 eV. The band gap of CdGa$_2$Se$_4$ is a smooth function of pressure and reaches a maximum of 1.42 eV at 50 kbar. In both compounds, the band gap is direct at Γ over the whole range of pressures.

3. Conclusions

This paper casts a reasonable doubt on whether CdGa$_2$S$_4$ and CdGa$_2$Se$_4$ disorder under pressure; it also provides the pressure dependence of the band gap to clarify the issue. A previous experiment measured the vibrational spectra of CdGa$_2$S$_4$ and CdGa$_2$Se$_4$ under
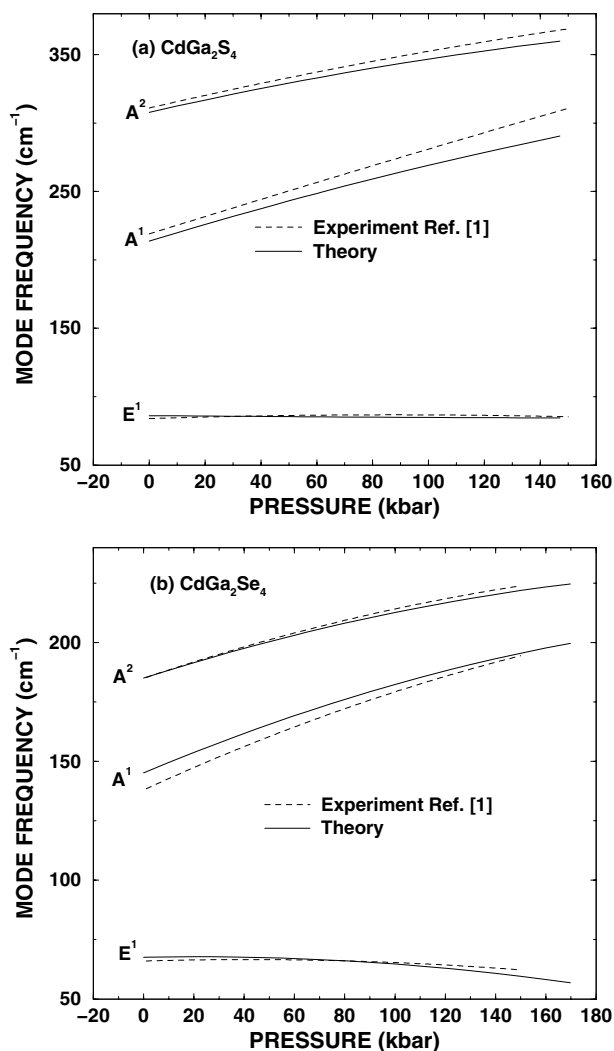
Figure 4. Comparison between the theoretical and experimental pressure dependences of the vibrational modes E^1, A^1, and A^2. (a) $CdGa_2S_4$, (b) $CdGa_2Se_4$.

pressure and concluded that these materials disorder under pressure on the basis of the softening of the E^1 mode and on the decreasing and broadening of the intensity peaks of the modes A^1 and A^2. In this paper, the vibrational spectra under pressure were calculated via an *ab initio* technique and, although $CdGa_2S_4$ and $CdGa_2Se_4$ were not disordered, the complete theoretical and experimental vibrational spectra are in good agreement overall. Although the intensity peaks were not calculated, the fact that theory and experiment agree as regards the dependence on pressure of the modes E^1, A^1, and A^2 leads one to question whether the disordering is happening. This can be clarified by examining the pressure dependence of the band gap. In this study, the band gap of $CdGa_2S_4$ is not a smooth function of pressure while the band gap of $CdGa_2Se_4$ is. The pressure dependence of the band gap could be measured experimentally and compared to the results here. If the comparison is good, one would think that the disordering was not happening. If the comparison is not good, the issue would be more complicated
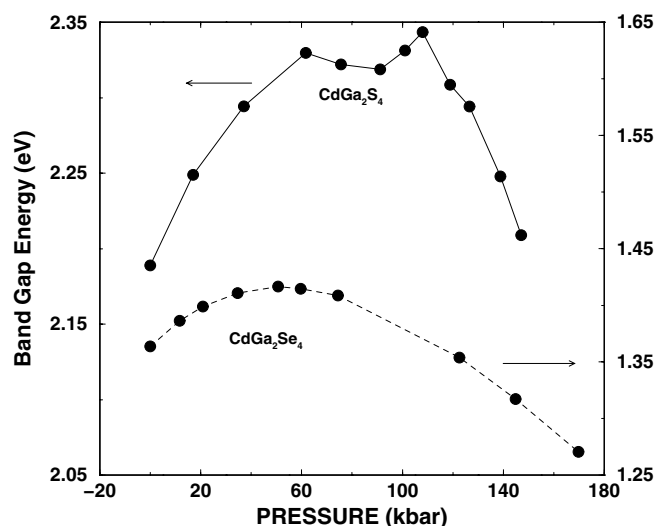
Figure 5. Pressure dependences of the LDA band gaps of CdGa$_2$S$_4$ and CdGa$_2$Se$_4$. The left and right axes represent the band gaps for CdGa$_2$S$_4$ and CdGa$_2$Se$_4$, respectively (as shown by ← and → in the plot). At zero pressure, the band gap of CdGa$_2$S$_4$ is 2.19 eV. Panyutin *et al* [19] studied the electronic properties of CdGa$_2$S$_4$ with an empirical pseudopotential method and obtained a direct band gap at Γ of 3.43 eV. The experimental results range from 3.40 to 3.8 eV [20]. At zero pressure the band gap of CdGa$_2$Se$_4$ is 1.36 eV. Panyutin *et al* [19] obtained a direct band gap at Γ of 2.44 eV; the experimental results range from 2.27 to 2.7 eV [20].

and would merit more research. The findings in this paper are relevant in the context of A^{II}B$_2^{III}$C$_4^{VI}$ materials where the disordered transitions found in CdGa$_2$S$_4$ and CdGa$_2$Se$_4$ were first predicted. In fact, ZnGa$_2$S$_4$ and ZnGa$_2$Se$_4$ have been found to disorder under pressure like CdGa$_2$S$_4$ and CdGa$_2$Se$_4$. In the future, I plan to study the dependence on pressure of the band gap and vibrational spectra of ZnGa$_2$S$_4$ and ZnGa$_2$Se$_4$.

Acknowledgments

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