Density functional study of the structure, thermodynamics and electronic properties of

CdGeAs$_2$

Density functional study of the structure, thermodynamics and electronic properties of CdGeAs$_2$

Peter Zapol†, Ravindra Pandey†, Max Seel†, J Manuel Recio‡ and Melvin C Ohmer§

† Department of Physics, Michigan Technological University, Houghton, MI 49931, USA
‡ Departamento de Química Física y Analítica, Universidad de Oviedo, 33006-Oviedo, Spain
§ Air Force Research Laboratory, Dayton, OH 45433, USA

Abstract. Structural, thermodynamic and electronic properties of CdGeAs$_2$ with chalcopyrite structure are investigated in the framework of density functional theory. We employ the linear combination of atomic orbitals method with the Gaussian basis sets and present the results for the equation of state, the Grüneisen constant, the electronic band structure and the pressure coefficients of the valence and conduction levels in CdGeAs$_2$.

1. Introduction

There has been considerable interest in cadmium germanium arsenide (CdGeAs$_2$) due to its suitability for non-linear optical applications in the infrared region. It has the highest non-linear optical coefficient, 236 pm V^{-1}, known for a phase-matchable compound semiconductor [1–4]. Additionally, it has a wide transparency region extending across the infrared from 2.4 to 18 μm. Recent successes [5] in the horizontal-gradient freeze growth technique made it possible to grow large single crystals of CdGeAs$_2$ which has led to renewed efforts to utilize this material for frequency doubling carbon dioxide laser emission lines from 9.3 to 10.6 μm (i.e., for second-harmonic generation).

Since the first CdGeAs$_2$ crystals were grown [6] in the early 1970s, their bulk properties have attracted much attention. Photoluminescence studies have revealed detailed information about the nature of the band gap [7]. Electrical and Hall effect measurements have determined the nature of the charge carriers in this material [8, 9]. The presence of at least two native acceptors has been observed in experiments utilizing radiation damage [10], magnetic resonance [11] and thermal admittance spectroscopy [12] techniques. The bulk modulus and Debye temperature were also obtained from measurements of the ultrasonic wave velocities [13]. On the theoretical front, empirical pseudopotential calculations have focused only on its band structure [15, 16]. Although calculations based on first-principles methods have been performed on several members of the chalcopyrite group [17, 18], we are not aware of any such calculations on CdGeAs$_2$.

In this paper, we report the results of calculations based on the density functional theory for CdGeAs$_2$ with the following aims: (i) to provide detailed information about its electronic structure; (ii) to determine its thermodynamic properties within a Debye-like model; and (iii) to combine knowledge of the electronic structure and thermodynamics to determine the pressure

         4517

dependence of its band structure. In the following section, computational details will be given. The results will be discussed in section 4.

2. Computational details

The electronic structure calculations for $CdGeAs_2$ are based on the density functional theory embedded in the CRYSTAL95 program [19] which has been successful in describing bulk and surface properties of covalent materials such as Si and GaN [20, 21]. We perform calculations in the framework of the local density approximation [22, 23] (LDA) to the density functional theory (DFT). In some cases, gradient-corrected functionals (GGA)—those of Becke [24] for exchange and Perdew and Wang [25, 26] for correlation—are employed to see the effect of these corrections on the calculated structural properties.

A linear combination of Gaussian orbitals is used to generate a localized atomic basis from which Bloch functions are constructed by a further linear combination with plane-wave phase factors. To reduce the computational cost in the present work, we represent the core electrons by Steven's effective core potentials (ECPs) [27, 28] and describe the respective valence electrons by the corresponding Gaussian basis set. The core electrons for Cd, Ge and As are $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ and $3d^{10}$. It has been shown that the ECPs (such as for Zn and Ge used in this work) derived from the Hartree–Fock calculations provide a satisfactory description of the ground-state properties in the DFT calculations [29]. The Gaussian basis set consists of four s, four p and three d-type shells for Cd (i.e. a 4121/4121/311 set), two s, two p and a d-type shell for Ge (i.e. a 41/41/1 set), and two s, two p and a d-type shell for As (i.e. a 41/41/1 set). It is to be noted here that the outermost 4d electrons of Cd are considered explicitly here as valence electrons and are not included in the ECPs. Furthermore, the outer exponents in each of the basis sets are reoptimized to yield the minimal total energy at the experimental geometry of $CdGeAs_2$.

The initial configuration for the geometry optimization is taken from the x-ray diffraction data. At ambient conditions, $CdGeAs_2$ crystallizes in the chalcopyrite phase [30, 31] with a space group of $I\bar{4}2D$. It can be constructed [7] by first considering a superlattice of the (cubic) zinc-blende phase with $c/a = 2$, replacing half of the cations by Cd ions and the other half by Ge ions and finally introducing a small distortion along the z-axis leading to $c/a = 1.889$. Furthermore, the As atoms are placed in the lattice in the special positions given by the internal parameter, u, which is related to the tetragonal distortion (i.e. $2 - (c/a)$) in the lattice. Geometry optimization calculations in the LDA approximation therefore involve the following steps:

(a) for several fixed values of the crystallographic unit-cell volume, ranging approximately from 0.8 to 1.08 times the experimental one, the lattice constant a and the internal parameter u are optimized with accuracies better than 10^{-3} Å and 10^{-4}, respectively;

(b) the calculated potential energy surface (i.e. total energy versus volume) is then used to obtain the optimized value of the unit-cell volume; and

(c) the optimization of a and u is again performed at this volume to get the values of the equilibrium structural parameters.

In the GGA calculations, geometry optimization is achieved by a less exhaustive approach where series of one-dimensional searches are performed varying each structural parameter (i.e. a, c and u) one by one at each step, repeating the steps until convergence to within 0.01 Å in the parameter value is achieved. In all of these calculations, the tolerance on the total-energy convergence in the iterative solution of the Kohn–Sham equations is set to 10^{-6} Hartree and a

grid of 59 k-points was used in the irreducible Brillouin zone for integration in the reciprocal space [32].

3. Results and discussion

3.1. Structural and electronic properties

The calculated equilibrium values of the structural parameters, namely a, c/a and u, for CdGeAs$_2$ are 5.914 Å, 1.915 and 0.265 in the LDA approximation and 5.94 Å, 1.89 and 0.265 in the GGA approximation respectively. On the other hand, the experimental values of the lattice parameters [31], a and c, are 5.9432 Å and 11.2163 Å respectively at 298 K leading to the c/a ratio of 1.887. Comparison between the GGA and experimental values of the lattice constants shows an excellent agreement. The calculated LDA unit-cell volume is also well within 1% of the experimental value. However, the LDA calculations yield a slight underestimation of a and overestimation of the c/a ratio as expected. Both LDA and GGA values of the internal parameter u are lower than the experimental value of 0.2785. This is in accordance with the results of the LDA calculations for ZnGeP$_2$, CdSnP$_2$ and CdSnAs$_2$, where the calculated u is consistently lower than the corresponding experimental value [18]. It is to be noted here that the x-ray diffraction studies obtain the value of the internal parameter, u, only in an indirect way [7].

The calculated Cd–As and Ge–As interatomic distances are 2.579 and 2.474 Å at the LDA level and 2.581 and 2.477 Å at the GGA level, respectively. It has been suggested that the tetrahedral angle in the chalcopyrite lattice is generally conserved by the group-IV atom (i.e. Ge). This results in a larger separation between the group II and the group V atoms relative to the group IV and the group V atoms in the lattice. This is what has been predicted by our calculations for CdGeAs$_2$. Assuming the conservation of tetrahedral bond radii, Jaffe and Zunger [33] have reported the structural coordinates of chalcopyrites. In this scheme, the calculated Cd–As and Ge–As distances turn out to be 2.63 and 2.45 Å respectively. We note here that the LDA calculations [18] for CdSnAs$_2$ yield a Cd–As distance of 2.611 Å.

Figure 1 displays the upper valence and lower conduction band structure of CdGeAs$_2$ calculated at the LDA equilibrium geometry. The total and partial densities of states of the
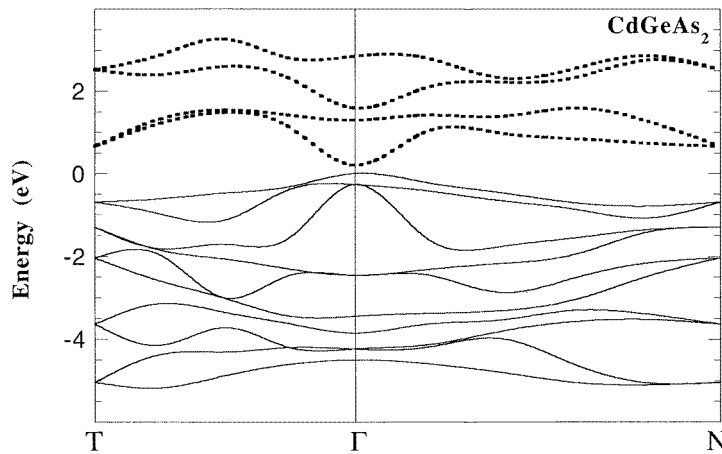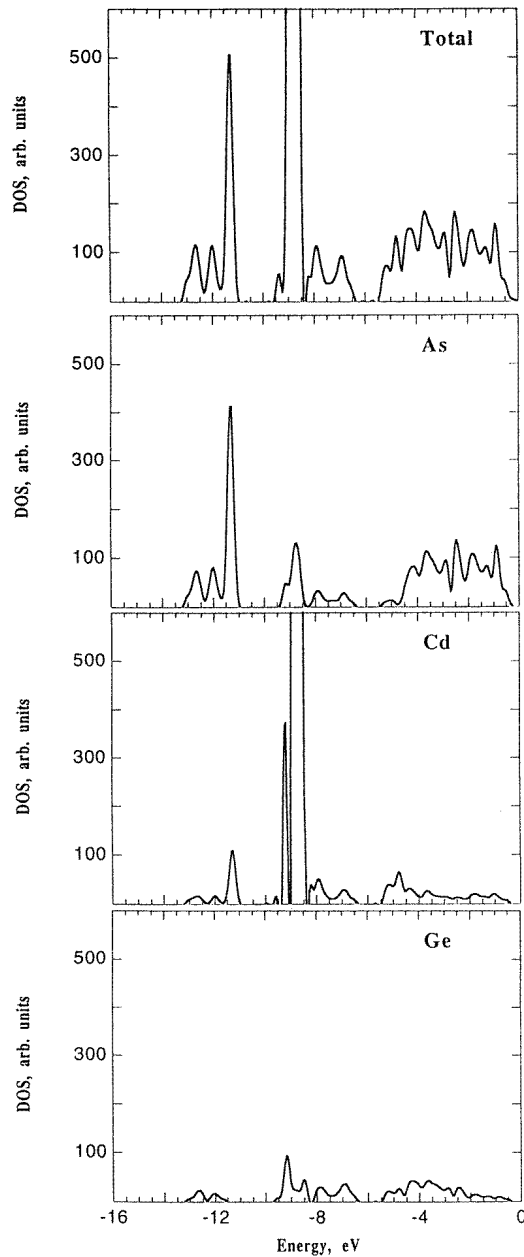

Figure 1. The electronic band structure of CdGeAs$_2$.

Figure 2. Total and projected densities of states of CdGeAs$_2$.

valence band are shown in figure 2. Accordingly, the upper valence band is mainly formed by the As p states with very small admixture of the Ge p states and the Cd p states (figure 2). This band has a width of about 5.5 eV. In the absence of the spin–orbit interaction terms in the present work, the top of the valence band consists of two levels having symmetry Γ_{5v} and Γ_{4v}, the former being doubly degenerate. The two levels originate from the same triply degenerate Γ_{15} level of the sphalerite structure. The difference between the Γ_{5v} and Γ_{4v} levels is referred

to as the crystal-field splitting (Δ_{cf}) which is calculated to be 0.33 eV. The corresponding experimental value is reported to be 0.21 eV [7].

At about 9 eV below the top of the valence band (figure 2), a relatively narrow Cd 4d band overlaps with the band representing the bonding between the Ge and As in the lattice. Interestingly, the LDA calculations [18] for CdSnP$_2$ reported the Cd 4d band to be at about -8.5 eV relative to the valence band maximum. However, we note here that the DFT calculations in the absence of self-interaction correction tend to underestimate the location of the d band with reference to the top of the valence band. Figure 2 also shows a band at about -11 eV attributed mainly to the As s orbitals which appear to be hybridized with the Cd and Ge orbitals. Relative to the valence band maximum, we have collected the energies of the electronic states at Γ, T and N k-points [7] which correspond to maxima and minima of the valence and conduction bands in table 1.

Table 1. Valence band energies in eV at Γ, T, N k-points [7] in the Brillouin zone of CdGeAs$_2$.

Level	
As p band maxima	
Γ_{4v}	0.00
Γ_{5v}	-0.33
$T_{3v} + T_{4v}$	-1.26
N_{1v}	-0.72
As p band minima	
Γ_{4v}	-4.49
$T_{4v} + T_{5v}$	-3.86
N_{1v}	-5.06
Ge–As band	
Γ_{4v}	-7.05
Γ_{2v}	-9.44
T_{5v}	-7.50
N_{1v}	-7.52
Cd d band	
Γ_{max}	-8.24
Γ_{min}	-8.85
T_{max}	-8.40
T_{min}	-8.72
N_{max}	-8.50
N_{min}	-8.90
As s band	
Γ_{5v}	-11.04
Γ_{3v}	-11.09
Γ_{1v}	-13.10
$T_{1v} + T_{5v}$	-11.09
T_{5v}	-12.34
N_{1v}	-11.23
N_{1v}	-12.19

In contrast to a very reasonable description of the valence states, the one-electron solutions of Kohn–Sham equations corresponding to the states in the conduction band are not known to

be reliable. The most evident and well-known discrepancy is a severe underestimation of the forbidden band gap. For example, the calculated band gap in the present work for $CdGeAS_2$ is 0.16 eV as compared to the experimental value of 0.61 eV. This discrepancy may be corrected by employing a semiempirical correction [34] which simply shifts states in the conduction band using the following equation:

$$\Delta = \frac{9 \text{ eV}}{\varepsilon_\infty} \tag{1}$$

where ε_∞ is the high-frequency dielectric constant of the material. For $CdGeAS_2$, ε_∞ is about 11.0 [1, 2, 14] leading to a value of the gap of 0.98 eV (table 2).

Table 2. The minimum-energy direct and pseudo-direct band gaps and crystal-field splittings (in eV) for $CdGeAs_2$.

	DFT gap	Corrected gap	Experiment
E_{direct}	0.16	0.98	0.61[a]
$E_{\text{pseudo-direct}}$	1.16	1.98	—
Δ_{cf}	−0.33	—	−0.21

[a] Reference [7].

The lowest gap between top of the valence band and the bottom of the conduction band is found to be at Γ. Thus, the present DFT calculations predict the gap to be direct (Γ_{4v}–Γ_{1c}) in agreement with experimental and empirical pseudopotential studies [15]. The ordering of states in the conduction band (i.e. $\Gamma_{1c} < \Gamma_{3c} < \Gamma_{2c}$) is also correctly predicted. We note here that experimental assignments are only tentative because transitions to the last two states are only weakly allowed.

3.2. Thermodynamic properties

To determine thermodynamic properties of $CdGeAs_2$, we have used a quasi-harmonic Debye-like model in which the Debye temperature, Θ, depends only on the volume of the crystal. It is a non-empirical model that only needs the knowledge of the potential energy surface (i.e. a set of computed $(V, E_{\text{latt}}(V))$ points) to generate the equation of state (EOS) and a number of related quantities for a given material. It is relevant to notice that whereas the key parameters from the experimental point of view are pressure (p) and temperature (T), the appropriate variable for controlling the computation is the volume (V). The computational strategy therefore includes optimization of the lattice constant a and the internal parameter u for several fixed values of the unit-cell volume to obtain the energy surface (see section 2). Figure 3 shows such an energy surface for $CdGeAs_2$ calculated using the LDA approximation.

Assuming isotropic conditions, Θ can be given by [35]

$$\Theta = \frac{\hbar}{k_B} \left[6\pi^2 V^{1/2} r \right]^{1/3} \sqrt{\frac{B_S}{M}} f(\sigma) \tag{2}$$

where $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, M the molecular mass of the compound, r the number of atoms per molecular unit, B_S the adiabatic bulk modulus of the crystal and σ the Poisson ratio which is taken to be 0.25, the value for the Cauchy solid [35]. The value of $f(\sigma = 0.25)$ then becomes 0.859 95. Note that the explicit expression for $f(\sigma)$ in equation (2) is [35]

$$f(\sigma) = \left\{ 3 \left[2\left(\frac{2}{3}\frac{1+\sigma}{1-2\sigma} \right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma} \right)^{3/2} \right]^{-1} \right\}^{1/3}. \tag{3}$$
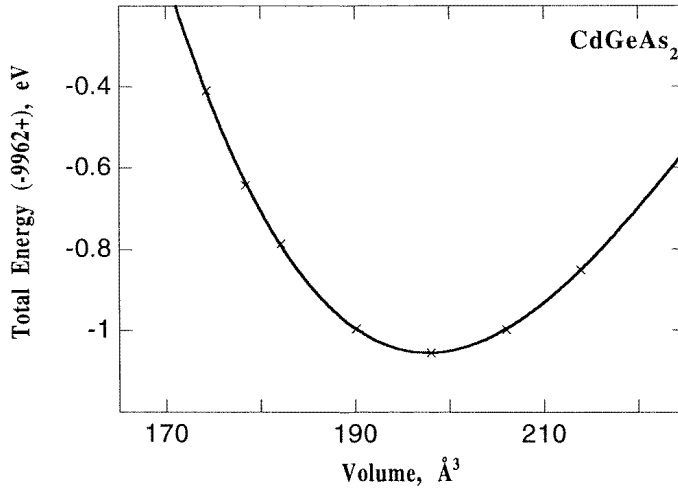
Figure 3. Total energy versus volume for CdGeAs$_2$ in the chalcopyrite phase.

In equation (2), B_S depends on V and T. In order to balance computational demand and accuracy, we further assume

$$B_S \simeq B_{\text{static}} = V\left(\frac{\mathrm{d}^2 E_{\text{latt}}(V)}{\mathrm{d}V^2}\right) \tag{4}$$

where B_{static} is the static bulk modulus.

Θ is now simply a function of V. It is also evident from equations (2) and (4) that there is no explicit consideration of the structural parameters in the volume derivatives, since we restrict consideration to hydrostatic conditions. This relevant feature of the model makes it fully independent of any particular crystal structure. Even if the crystal energy depends on many internal parameters and cell constants, a set of pairs (E_{latt}, V) is sufficient for employing the model. A more detailed description of the model is given in references [35, 36].

Our computed values of isothermal and adiabatic bulk moduli ($B_T(p = 0) = B_0$ and B_S) and their pressure and temperature derivatives are given in table 3 along with the available experimental data. Figure 4 shows the equation of state generated using the normalized $V(p)/V_0$ values, where V_0 is the corresponding equilibrium volume at zero pressure. It should be noted here that Hailing *et al* [13] used the experimental bulk modulus and its first derivative obtained at pressures up to 0.1 GPa from ultrasonic measurements as parameters and did not fit the equation of state to the experimental curve. The higher experimental value of 69.7 GPa of B_0 relative to the calculated one of 57.0 GPa makes the simulated crystal more compressible, as illustrated in figure 4.

Table 3. Bulk moduli and related properties of CdGeAs$_2$.

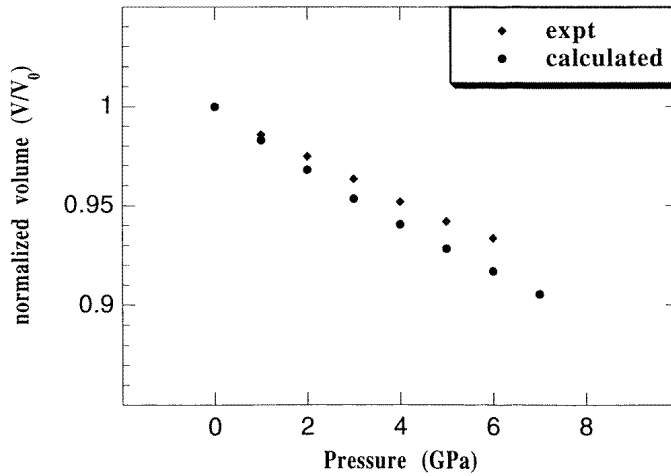|	B_0 (GPa)	B_S (GPa)	B_0'	B_0'' (GPa^{-1})
This work: 0 K	57.03	57.03	4.79	−0.32
This work: 300 K	53.21	54.43	5.47	−0.46
Experiment[a]: 300 K	69.7	—	6.18	—

[a] Reference [13].

Figure 4. The equation of state of CdGeAs$_2$.

In the quasi-harmonic model used here, the Debye temperature, Θ_D, turns out to be 273 K at the static equilibrium and 269 K at room temperature. This variation is due to change of equilibrium volume with temperature. On the other hand, the specific heat measurements [37] made between 2 K and 30 K determine Θ_D to be 230 K whereas the ultrasonic wave velocity experiment [13] yields the value of 257 K for Θ_D.

We note here that the thermodynamic properties that are especially sensitive to computational details are those related to the volume dependence of Θ, since they involve third derivatives of the static lattice energy. The most important factor in computing this set of properties is the Grüneisen constant, γ. Our calculations yield a value of γ of 2.262 at 300 K for CdGeAs$_2$. For the volume thermal expansion coefficient, α, the calculated values are 30.9×10^{-6} K^{-1} at 300 K and 33.8×10^{-6} K^{-1} at 400 K, as compared to the experimental value of 18×10^{-6} K^{-1}.

The optical transitions in chalcopyrites are sensitive to the applied hydrostatic pressure, leading to a dependence of the pressure coefficients on the nature of the band gap. For example, it has been found [38] that the pseudo-direct-gap chalcopyrites [39], such as ZnGeP$_2$, have a small positive or negative slope of the absorption edge, while CdGeAs$_2$ and other direct-gap chalcopyrites have a large positive slope. Although the LDA calculations do not provide very good quantitative predictions of the band gap, they do provide reliable predictions of the change in gap under hydrostatic conditions. For CdGeAs$_2$, we find that both the valence and conduction levels at T, N and Γ k-points in the Brillouin zone show a linear variation with applied pressure up to 10 GPa. The calculated pressure coefficients [40] of these levels are given in the table 4, and yield a coefficient of the minimum-energy direct gap (Γ_{4v}–Γ_{1c}) of 9.5×10^{-6} eV bar^{-1}. It is in very good agreement with the experimental value [41] of 9.3×10^{-6} eV bar^{-1}. It is thought that knowledge of the pressure coefficients for different levels would assist experimentalists in identifying various optical transitions in CdGeAs$_2$.

In summary, we have calculated lattice constants, the equation of state, the Debye temperature, the Grüneisen constant and the electronic band structure of CdGeAs$_2$ in the chalcopyrite structure, and these are in very good agreement with the available experimental data. The calculated results have also provided details of the valence and conduction bands, predicting their variation with pressure.

Table 4. Pressure coefficients in (10^{-6} eV bar^{-1}) of valence and conduction levels of CdGeAs$_2$.

Level	
Γ_{5v}	0.9
Γ_{4v}	6.5
Γ_{3c}	−2.9
Γ_{1c}	16
T_{3v+4v}	−0.87
T_{5c}	2.2
N_{1v}	2.6
N_{1c}	8.4

Acknowledgment

Note added in proof. Recently, Rashkeev, Limpijumnong and Lambrecht [42] have reported the band structure of CdGeAs$_2$ at the experimental values of the structural parameters. Their calculations were based on the linear muffin-tin orbitals (LMTO) method within the atomic sphere approximation (ASA). Although the gap was found to be negative at the LDA level, semiempirical corrections to the conduction band states yielded a gap of 1.01 eV.

References

[1] Byer R L, Kildal H and Feigelson R S 1971 *Appl. Phys. Lett.* **19** 237
[2] Kildal H 1972 *Report* AFML-TR-72-277 (Government technical report available from NTIS, AD739556)
[3] Boyd G D, Buehler E, Storz F and Wernick J H 1972 *IEEE J. Quantum Electron.* **8** 419
[4] Dmitriev V G, Gurzadayan G G and Nikogosyan D N 1997 *Handbook of Nonlinear Optical Crystals* (New York: Springer)
[5] Schunemann P G and Pollak T M 1997 *J. Cryst. Growth* **174** 215
[6] Kesamanly F P and Rud' Yu V 1993 *Semiconductors* **27** 969
[7] Shay J L and Wernick J H 1974 *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications* (Oxford: Pergamon)
[8] Fischer D W, Ohmer M C and McCrae J E 1997 *J. Appl. Phys.* **81** 3579
[9] Rud V Yu and Rud' Yu V 1993 *Japan. J. Appl. Phys. Suppl.* 3 **32** 672
[10] Brudnyi V N, Krivov M A, Potapov A I, Polushina I O K, Prochukhan V D and Rud' Yu V 1978 *Phys. Status Solidi* a **49** 761
[11] Halliburton L E, Edwards G J, Schunemann P G and Pollak T M 1994 *J. Appl. Phys.* **77** 435
[12] Smith S R, Evwaraye A O and Ohmer M C 1998 *MRS Proc. on Infrared Applications of Semiconductors II* vol 484 (Pittsburgh, PA: Materials Research Society) p 581
[13] Hailing Tu, Saunders G A, Lambson W A and Feigelson R S 1982 *J. Phys. C: Solid State Phys.* **15** 1399
[14] Pandey R, Ohmer M and Gale J D 1998 *J. Phys.: Condens. Matter* **10** 5525
[15] Polygalov Yu I and Poplavnoi A S 1981 *Izv. VUZ Fiz.* **12** 78
[16] Madelon R, Paumier E and Hairie A 1991 *Phys. Status Solidi* b **165** 435
[17] Jaffe J E and Zunger A 1984 *Phys. Rev.* B **30** 741
[18] Continenza A, Massidda S, Freeman A J, de Pascale T M, Meloni F and Serra M 1992 *Phys. Rev.* B **46** 10 070
[19] Dovesi R, Saunders V R, Roetti C, Causà M, Harrison N M, Orlando R and Aprà E 1996 *CRYSTAL95 User's Manual* Universidad de Torino
[20] Pandey R, Causà M, Harrison N M and Seel M 1996 *J. Phys.: Condens. Matter* **8** 3993
[21] Pandey R, Zapol P and Causà M 1997 *Phys. Rev.* B **55** 1
[22] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[23] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[24] Becke A D 1988 *Phys. Rev.* A **38** 3098
[25] Perdew J P and Wang Y 1986 *Phys. Rev.* B **33** 8800
[26] Perdew J P and Wang Y 1989 *Phys. Rev.* B **40** 3399
[27] Stevens W J, Basch H and Krauss M 1985 *J. Chem. Phys.* **81** 6026

[28] Stevens W J, Krauss M, Basch H and Jasien P G 1992 *Can. J. Chem.* **37** 2659
[29] Causà M and Zupan A 1994 *Int. J. Quantum Chem.* **S28** 633
[30] Borshchevskii A S, Goryunova N A, Kesamanly F P and Nasledov D N 1967 *Phys. Status Solidi* **21** 9
[31] Abrahams S C and Bernstein J L 1974 *J. Chem. Phys.* **61** 1140
[32] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5118
[33] Jaffe J E and Zunger A 1984 *Phys. Rev.* B **29** 1882
[34] Fiorentini V and Baldereschi A 1992 *J. Phys.: Condens. Matter* **4** 5967
[35] Poirier J P 1991 *Introduction to the Physics of the Earth's Interior* (Cambridge: Cambridge University Press)
[36] Francisco E, Recio J M, Blanco M A, Pendas M A and Costales A 1998 *J. Phys. Chem.* A **102** 1595
[37] Bohmhammel K, Deus P and Schneider H A 1981 *Phys. Status Solidi* a **65** 563
[38] Shileika A 1974 *Surf. Sci.* **73** 730
[39] In $ZnGeP_2$, the conduction band minimum and the valence band maximum is at Γ. Note that $ZnGeP_2$ has a binary analogue GaP which has the minimum of the conduction band at X. The X point of the zinc-blende structure corresponds to the Γ point in the chalcopyrite Brillouin zone making the gap direct. A band gap of this nature is referred to as *pseudo-direct*.
[40] The pressure coefficients of valence and conduction levels are calculated from the variation of their energies with pressure.
[41] Bendorius R A, Prochukhan V D and Shileika A 1972 *Phys. Status Solidi* b **53** 745
[42] Rashkeev S N, Limpijumnong S and Lambrecht W R L 1999 *Phys. Rev.* B **59** 2737