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1994 J. Phys.: Condens. Matter 6 9875

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# *Ab initio* calculation for MgTe and transition of $\text{Mg}_x\text{Cd}_{1-x}\text{Te}$ from direct to indirect semiconductor

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Received 21 July 1994, in final form 27 September 1994

**Abstract.** The ternary mixed crystal system  $\text{Mg}_x\text{Cd}_{1-x}\text{Te}$  has recently attracted interest as a basic material for the blue laser diode. We use norm-conserving pseudopotentials in connection with the local-density approximation for *ab initio* calculations of the stable crystal structure and the lattice constant. Our results are in quantitative agreement with structural properties. The electronic band structure is calculated in dependence on the composition  $x$  of the system by the virtual-crystal approximation (VCA). We find a transition from direct to indirect energy gap for  $x = 0.7$  in accordance with experimental data.

## 1. Introduction

In material science ternary mixed crystal systems are frequently used for band-structure engineering. Zn- and Cd-based II-VI compounds offer direct band gaps through the entire visible spectral range to the ultraviolet. In particular the mixed crystal systems  $\text{ZnSe}_x\text{Te}_{1-x}$ , CdS are basic materials to fabricate light emitting diodes (LEDs) [1, 2, 3, 4] and semiconductor lasers [1, 2, 3, 4] in the blue/green part of the spectrum (see figure 1). The lattice mismatch between components of these systems requires special care in growing layered structures and is one possible reason for the still short lifetime of the devices [3].

The ternary system  $\text{Mg}_x\text{Cd}_{1-x}\text{Te}$  offers some advantages. With its lattice constant almost independent of  $x$  (as in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ) lattice-matched quantum wells can be grown with CdTe as well material (figure 1). In connection with the larger band gap of MgTe such structures can be designed to operate even in the ultraviolet range [5, 6, 7, 8]. CdTe exhibits many interesting features: a band gap in the middle of the solar spectrum, a high atomic weight for x-ray detection and an electro-optic coefficient which is about a factor of four higher than in GaAs [9, 10].

*Ab initio* calculations are quite numerous for CdTe [11, 12, 13, 14], but have been performed only once for MgTe using the plane-wave non-local-pseudopotential method [15]. These results will be reported later in this paper for comparison. Recent MBE-grown samples of  $\text{Mg}_x\text{Cd}_{1-x}\text{Te}$  [10, 5] reveal the stability of the zincblende structure for all  $x$  and a transition from a direct- to an indirect-gap semiconductor with increasing  $x$ .

The total energy as a ground-state property of a many-particle system can be calculated by applying the concepts of density-functional theory (DFT), which usually is evaluated in the local-density approximation (LDA) [16]. For crystalline solids pseudopotentials and plane-wave expansions of the wave functions have been used successfully to describe the fundamental properties of semiconductors of zincblende or of other structures [17]. We use smooth norm-conserving pseudopotentials [17, 18] generated in a scheme proposed

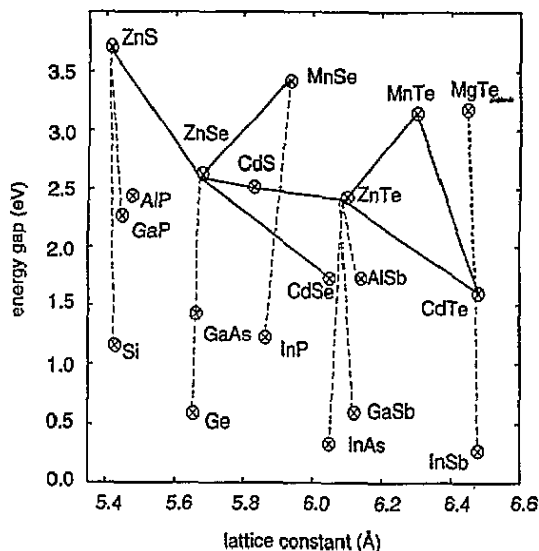


Figure 1. Band gap of several semiconductors versus lattice constant (MgTe in zincblende structure).

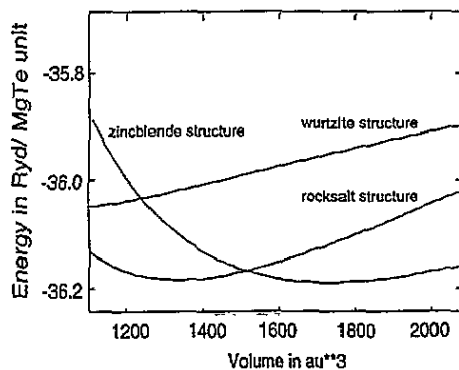


Figure 2. Total energy  $E$  versus volume  $V$  for rocksalt, zincblende and wurtzite structures at  $T = 0$  K for MgTe.

recently by Troullier and Martins [18]. The mixed-crystal aspects are considered within the virtual-crystal approximation (VCA) by mixing the anion pseudopotentials according to the composition parameter  $x$ . The VCA is the first-order method of calculation for a mixed crystal [4], which works well and is adequate in computing the transition from direct to indirect semiconductor.

A brief outline of the method (DFT and LDA) for calculating the total energy of the crystal ground state and for computational details is given in refs. [11, 19]. The exchange-correlation potential is taken from [20].

In section 2 we discuss structural properties of MgTe and of CdTe and compare our results with experimental data. In section 3 we present results of the electronic properties (band structure, density of states) of  $Mg_xCd_{1-x}Te$ , which include the transition from a direct (CdTe) to an indirect semiconductor (MgTe).

## 2. Structural properties

Within *ab initio* DFT-LDA calculations the structural properties (crystal structure, equilibrium lattice constant, bulk modulus) come first. Results of such calculations for CdTe are reported in the literature [11, 12, 13, 14] and are given here in table 1 for the zincblende structure which (under normal conditions) is the stable one. In these calculations the d electrons have been considered as valence electrons [11, 13].

For the second binary compound MgTe we have calculated total energies versus volume for three possible crystal structures: zincblende, wurtzite and rocksalt. The calculated total energies were interpolated using Vinet's equation of state (for details see [11, 22, 23]). The results in figure 2 show that at  $T = 0$  K (for which all our calculations are done) zincblende is the most stable structure and that the wurtzite structure has an even higher ground-state energy than the rocksalt structure. According to our calculations MgTe would change under hydrostatic pressure from zincblende to rocksalt as known for other II-VI semiconductors (see table 1).

**Table 1.** Equilibrium parameters of CdTe (the 3d electrons are valence electrons (+d) or frozen in the core (-d)); comparison of calculated values with experiment.

Zincblende	$a_0$ (au)	$B$ (kbar)
CdTe ((+d) present)	12.19	442
CdTe ((-d) [13])	11.83	512
CdTe [31, 32] (experiment)	12.24	445
CdTe [14] (LMTO)	11.94	417
CdTe [28] (FLAPW)	12.22	462
CdTe [12] (LAPW)	12.22	440

**Table 2.** Equilibrium parameters of MgTe; comparison of calculated values with experiment.

	$a_0$ (au)	$c/a$	$B$ (kbar)
<b>Rocksalt</b>			
MgTe (present)	11.02		533
MgTe [15] (calculated)	11.04		
<b>Zincblende</b>			
MgTe (present)	12.00		376
MgTe [15] (calculated)	12.02		
MgTe [5, 10] (experiment)	12.0		
<b>Wurtzite</b>			
MgTe (present)	8.557	1.634	325
MgTe [15] (calculated)	8.513	1.633	
MgTe [5] (experiment)	8.579	1.627	
MgTe [21] (experiment)	8.54	1.633	

Earlier experimental data report the wurtzite structure as the stable one for MgTe [24]. These samples (hygroscopic non-stoichiometric mixture Mg+MgO+MgTe) were grown at high temperatures. In contrast the more recent low-temperature MBE-grown samples [5, 10] favour zincblende as the stable structure for the whole composition range  $x$  of  $Mg_xCd_{1-x}Te$ .

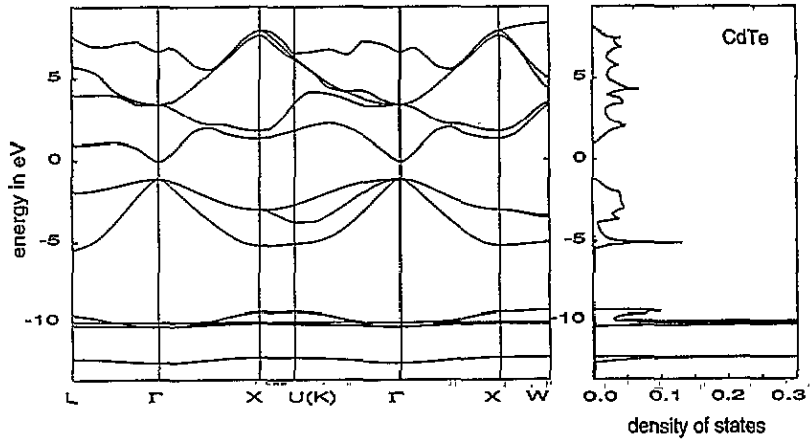


Figure 3. Electronic band structure and density of states of CdTe in the zincblende structure with the density of states at the equilibrium lattice constant  $a_0 = 12.19$  au.

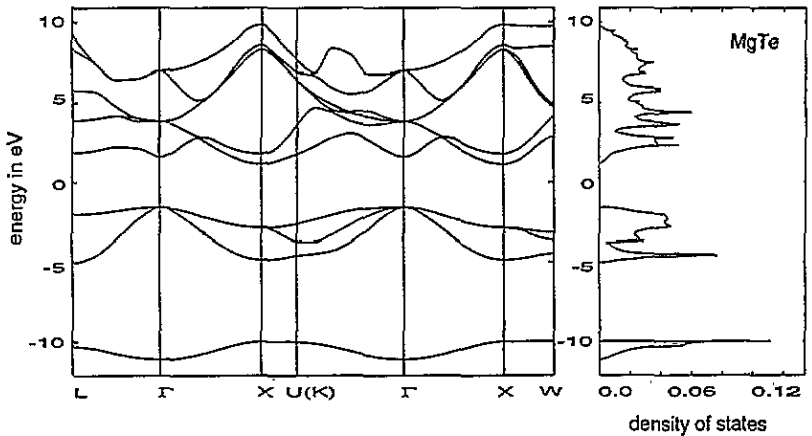


Figure 4. Electronic band structure and density of states of MgTe in the zincblende structure with the density of states at the equilibrium lattice constant  $a_0 = 12.00$  au.

### 3. Electronic properties

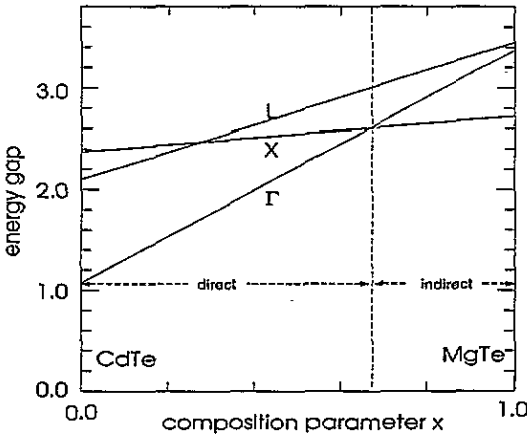
The band structure of CdTe shows all the well known features including the direct gap at the  $\Gamma$  point. Figures 3 and 4 show the electronic band structures and densities of states of CdTe and of MgTe in the zincblende structure. In contrast the smallest gap of MgTe is indirect with the lowest conduction-band minimum in X. It should be kept in mind that energy gaps from DFT-LDA calculations are usually smaller than the experimental values. Band-gap corrections, e.g. in the GW approximation, can account for this deficiency but usually turn out to be almost independent of  $k$  [25, 26, 27]. Therefore, conclusions concerning the direct-indirect transition using DFT-LDA results should essentially be correct.

Table 3 shows valence-band energies of the valence bands of CdTe. There is a good agreement of our calculation with other calculations and experiments except for the d bands. The role of the d electrons is discussed in [12, 13]. Figures 3 and 4 show that CdTe is a direct semiconductor and that MgTe is an indirect semiconductor. These theoretical results

**Table 3.** Valence-band energies of CdTe (in eV) in zincblende structure, comparison of calculated values with experiment and valence-band energies of MgTe (in eV) in the zincblende structure (energies in eV, maximum of valence band is at 0 eV).

	Experiment [28] CdTe	EPP [30] CdTe	FLAPW [28] CdTe	LAPW [12] CdTe	Present CdTe	Present MgTe
$\Gamma_6$	-10.0	-11.07	-11.59	-11.30	-11.17	-9.5
$\Gamma_7$	-10.65		-8.47	-8.43	-8.99	
$\Gamma_8$	-10.49		-8.28	-8.28	-8.75	
$L_6$		-9.64	-11.20	-10.91	-10.90	-8.7
$L_6, L_{4,5}$	$-0.9 \pm 0.3$	-0.65	-0.82	-0.80	-0.78	-0.5
$X_6$		-9.12	-11.08	-10.79	-10.83	-8.5
$X_7$	$-5.2, -4.7$	-5.05	-4.72	-4.44	-4.08	-3.3
$L_6$		-4.73	-4.82	-4.54	-4.30	-3.5
$X_6X_7$	-1.8	-1.60	-2.02	-1.92	-1.90	-1.3

are in accordance with experiments and with other calculations [14, 28, 12] for CdTe and with recent experiments [5, 10] for MgTe.



**Figure 5.** Direct ( $\Gamma$ ) and indirect ( $X, L$ ) band gap versus composition parameter  $x$  of  $Mg_xCd_{1-x}Te$  in the zincblende structure.

The energy bands of the ternary alloy  $Mg_xCd_{1-x}Te$  have been calculated within the VCA. It assumes a new quasilattice  $Mg_xCd_{1-x}$  on one sublattice, which is described by linear superposition of the ionic pseudopotentials of Mg and Cd. In contrast to Mg which has no d electrons in the core and for which a clear distinction of core and valence electrons is possible, we have to consider in Cd the 4d electrons explicitly as valence electrons, because of their overlap with the 5s electrons. Unfortunately no linear superposition is possible between ionic pseudopotentials with (5s<sup>2</sup>4d<sup>10</sup> Cd) and without d electrons (3s<sup>2</sup> Mg). In order to combine LDA and VCA calculations one has to consider the Cd 4d electrons in the core in spite of its overlap with the valence electrons. As a consequence the gap energy of CdTe gets too large [12, 29]. Nevertheless we have performed the VCA calculation to check for deviations of the band-edge energies from linear dependence on  $x$ . We took the absence of such deviations as justification for linear interpolation between the smallest band gaps of CdTe (with 4d electrons treated as valence electrons) and MgTe. The result (figure 5) shows a transition from a direct to an indirect gap at  $x = 0.7$  in close agreement with the

experimental finding [5].

## Acknowledgments

I thank S Baroni for numerical support, and U Rössler, A Waag, P Pavone and G H Grosch for useful discussions. This work has been performed with partial support from the Graduiertenkolleg 'Komplexität in Festkörpern: Phononen, Elektronen und Strukturen' and from the Bayerische Forschungsstiftung (FOROPTO).

## References

- [1] Haase M A, Qiu J, DePuydt J M and Cheng H 1991 *Appl. Phys. Lett.* **59** 1272
- [2] Kobayashi M, Minol N, Katagiri H, Kimura R, Konagai M and Takahashi K 1986 *Appl. Phys. Lett.* **48** 296
- [3] Neumark G F, Paark, R M and DePuydt J M 1994 *Phys. Today* **6** 26
- [4] Freytag B, Pavone P, Rössler U, Wolf K, Lankes S, Schötz G, Naumov A, Jilka S, Stanzi H and Gebhardt W *Solid State Commun.* at press
- [5] Waag A 1994 Private communication
- [6] Montegu B, Laugier A and Barbier D 1979 *Phys. Rev. B* **19** 1920
- [7] Belsyuk P P, Savitskii A V, Ilashchuk M I, Rusnak N I, Vlasjuk V I and Parfenyuk O A 1991 *Sov. Phys.-Semicond.* **25** 581
- [8] Dutt B V and Spitzer W G 1977 *J. Appl. Phys.* **48** 2107
- [9] Pankove J 1971 *Optical Processes in Semiconductors* (New York: Dover) p 346
- [10] Waag A, Heinke H, Scholl S, Becker C R and Landwehr G 1993 *J. Cryst. Growth* **131** 607
- [11] Freytag B, Grosch G H, Rössler U, Range K J and Karch K 1993 *J. Chem. Phys.* **99** 6751
- [12] Wei S H and Zunger A 1988 *Phys. Rev. B* **37** 8958
- [13] Grosch G H, Freytag B, Range K J and Rössler U 1994 *J. Quantum Chem.* at press
- [14] Agrawal B K and Agrawal S 1992 *Phys. Rev. B* **45** 8321
- [15] Yeh C Y, Lu Z W, Froyen S and Zunger A 1992 *Phys. Rev. B* **46** 10086
- [16] Dreizler R M and Gross E K U 1990 *Density Functional Theory—An Approach to the Quantum Many Body Problem* (Berlin: Springer)
- [17] Bachelet G P, Hamman D R and Schlüter M 1982 *Phys. Rev. B* **26** 4199
- [18] Troullier N and Martins J L 1991 *Phys. Rev. B* **43** 1993
- [19] Giannozzi P, de Gironcoli S, Pavone P and Baroni S 1991 *Phys. Rev. B* **43** 7231
- [20] Perdew J and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [21] Klemm W and Wahl K 1951 *Anorg. (Allg.) Chem.* **266** 289
- [22] Wellenhofer G, Karch K, Pavone P, Rössler U and Strauch D 1994 *J. Phys.: Condens. Matter* submitted
- [23] Freytag B 1994 *Dissertation* Regensburg
- [24] Zachariasen W 1928 *Z. Phys. Chem.* **128** 417
- [25] Hott R 1991 *Phys. Rev. B* **44** 1057
- [26] Hybertsen M S and Louie S G 1986 *Phys. Rev. Lett.* **55** 1418
- [27] Hybertsen M S and Louie S G 1986 *Phys. Rev. B* **34** 5390
- [28] Continenza A and Freeman A J 1991 *Phys. Rev. B* **43** 8951
- [29] Freytag B and Rössler U 1994 *J. Cryst. Growth* **138** 499
- [30] Chelikowsky J R and Cohen M L 1976 *Phys. Rev. B* **14** 556
- [31] Reisener A 1992 *Dissertation* Regensburg
- [32] *Landolt-Börnstein New Series* Group III, vol 22a (Berlin: Springer)