Pressure dependence of the optical absorption edge in $Cd_{1-x}Mn_xTe$

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Abstract. For the Mn-substituted CdTe semiconductors, the anomaly of the pressure coefficient of the optical absorption edge at about 2.0–2.3 eV with large concentration values, x, is studied by using the method of linear combinations of atomic orbitals. Results show that at the optical absorption edge, the p–d excitations may occur at higher Mn-concentrations and the pressure behaviour has a negative pressure effect similar to the Mn intra-d excitations. The physical reason for the negative pressure effect of the p–d transition is discussed and the numerically calculated result of the pressure coefficient for $Cd_{0.5}Mn_{0.5}Te$ is found to be in excellent agreement with the experimental data.

The diluted magnetic semiconductors of Mn-substituted II-VI compounds $A_{1-x}^{II}Mn_xC^{VI}$ exhibit a variety of interesting phenomena [1] of potential technological significance. $Cd_{1-x}Mn_xTe$ is probably the most extensively studied member of the $A_{1-x}^{II}Mn_xC^{VI}$ group. It crystallises in a single-phase zinc-blende (ZB) structure up to a composition of $x = 0.7$. The band gap increases [2] and the Mn–Te bond length decreases [3] slightly with added Mn. While there have been extensive experimental studies of bulk $Cd_{1-x}Mn_xTe$, some fundamental problems still remain. One of them is the nature of the anomaly of the optical absorption edge at approximation 2.0–2.3 eV when $x > 0.5$ which exhibits a concentration-independent behaviour [4–9] and a negative pressure coefficient [10]: it is yet unclear if it represents an intra-atomic impurity-like transition within the Mn $3d^5$ manifold [5–6] or an interband transition between the occupied Te 5p states and the empty Mn 3d states [7–9]. The pressure behaviour of the absorption edge is of interest in this work.

In this paper we present a theoretical study of the pressure behaviours of the electronic structures of $Cd_{1-x}Mn_xTe$, specifically $Cd_{0.5}Mn_{0.5}Te$. Our calculations are performed by using the extended Hückel theory [11]. The basis consists of s^2, p^6, d^{10} orbitals for the cation site atoms (Cd and Mn) and s^2, p^6 orbitals for the anion atoms (Te). Parameters were obtained by fitting to the first-principles calculated band structures of CdTe and MnTe (with a hypothetical antiferromagnetic (AF) zinc-blende structure [12]).

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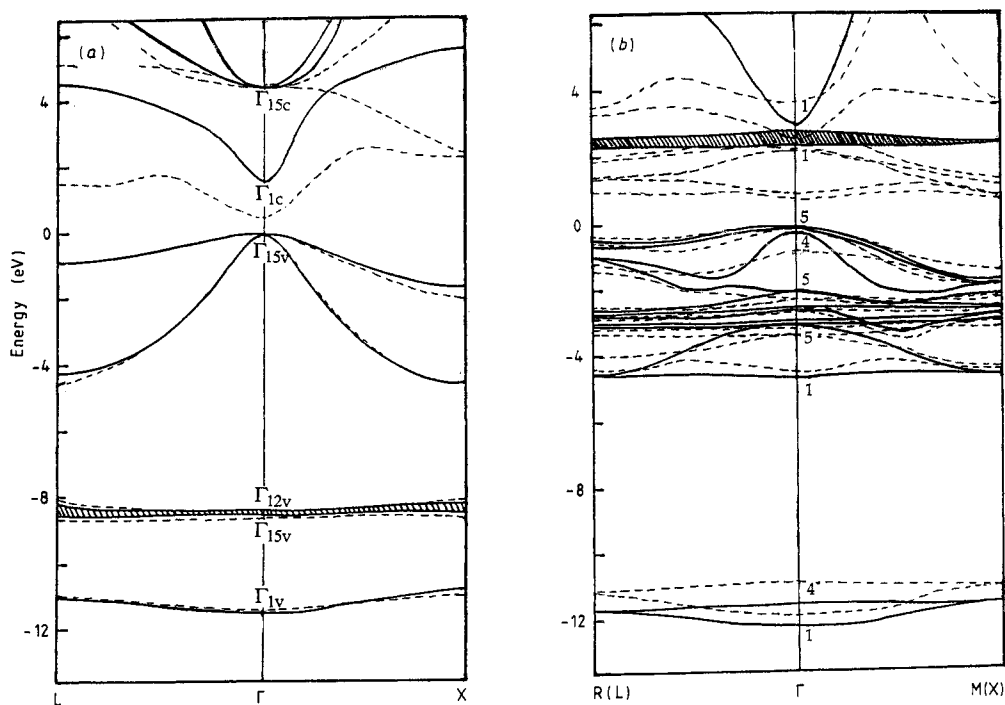
Figure 1. Fitted electronic band structures (full curves) to the results of LMTO calculations from [12] (broken curves) of (*a*) CdTe, and (*b*) AF ZB MnTe; the shaded areas denote the d electron bands.

The fitted band structures of CdTe and AF ZB MnTe are given in figure 1. As can be seen in figure 1, both the valence bands of CdTe and MnTe are fitted in good agreement with the first-principles calculations. While the conduction bands fitted here are much different from the results of [12]—where the energy gaps calculated from a local spin density functional (LSDF) approach are considerably smaller than that of the experimental values due to the one-electron potential—they do not contain the discontinuity [13] between the valence and conduction bands which must be present in the exact density functional potential. In our calculation, the 's-p' energy gaps of CdTe and MnTe are fitted as 1.6 eV and 3.1 eV, respectively, where the former is the experimental value and the latter is a rough extrapolation of the data from $x < 0.42$ to $x = 1$ which suggests a 'limiting MnTe phase' [12]. For computational convenience in the AF MnTe calculation, we have used the ordinary space group (instead of the magnetic one) by treating the two Mn atoms in the unit cell with opposite spins as two different types of atoms. This reduces the symmetry of the ZB structure from T_d^2 to D_{2d}^5(CuAu-I structure). Therefore, the R and M points (the edges of the Brillouin zone (BZ) of the D_{2d}^5 structure as indicated in figure 1(*b*)) correspond to the points L and X, respectively, of the FCC BZ. With these considerations, the states of different symmetry in the ZB structure can fold into states of the same symmetry as in the CuAu-I-like structure. In figure 1(*b*) the states at the Γ point in the CuAu-I-type structure are folded by the relations $\Gamma_1(\text{ZB}) \rightarrow \Gamma_1(\text{CuAu})$, $\Gamma_{15}(\text{ZB}) \rightarrow \Gamma_5 + \Gamma_4$, $X_1(\text{ZB}) \rightarrow \Gamma_4(\text{CuAu})$, etc. We shall describe the main features of the electronic structure of CdTe and AF ZB MnTe in the following.

In the band structures of CdTe (with bond length R(Cd–Te) = 2.80 Å) along the L–Γ–X line, the valence band can be divided into three parts: (i) the band centred at $E_v - 11.3$ eV (where E_v is the valence band maximum, VBM) which originates from the Te 5s orbitals; (ii) the narrow Cd 4d bands at $E_v - 8.5$ eV; and (iii) the upper Te 5p + Cd 5s valence band with a bandwidth of 4.6 eV. Whereas in the AF ZB MnTe (with bond length R(Mn–Te) = 2.73 Å) band structure along the R(L)–Γ–M(X) line (where L and X indicate the k-points in the ZB BZ), the electronic structure can be divided into: (i) the states lying between $E_v - 4.0$ eV and E_v are derived primarily from Mn majority-spin d levels and Te sp levels. Within the valence band, the states between $E_v - 2.0$ eV and E_v have the largest Te sp component but display strong p–d hybridisation effects; (ii) the states lying in the band $E_v + 2.5$ eV and $E_v + 2.9$ eV are derived primarily from unoccupied Mn minority-spin d levels. The lower part of the band is only slightly hybridised with the Te p levels, while the upper part of the band exhibits stronger p–d hybridisation effects; and (iii) the band above $E_v + 3.0$ eV corresponds to the conduction band in an ordinary sp-bonded semiconductor. The minimum at Γ contains roughly equal contributions from the s orbitals in the Mn atoms and Te atoms, and none from the Mn d orbitals. Our calculated unoccupied states in the AF ZB MnTe exhibit a global similarity to that of Larson *et al* [14], where the Mn 4s conduction band is found to be well above the unoccupied Mn 3d↓ states.

We have modelled the 50% ~ 50% $Cd_{1-x}Mn_xTe$ alloy by an antiferromagnetic ordered structure (space group D_{2d}^{12})ABC$_2$ (=CdMnTe$_2$) in a body-centred-tetragonal structure with eight atoms in the primitive cell, i.e. the chalcopyrite structure (see figure 2), in order to simulate the properties of the suggested AF ordered phase at $x > 0.60$ [1]. The atomic positions in the unit cell are given by

Cd: $R_{A_1} = (0, 0, 0)a$ $R_{A_2} = (0, \frac{1}{2}, \eta/4)a$

Mn1(↑): $R_{B_1} = (\frac{1}{2}, \frac{1}{2}, 0)a$ Mn2(↓): $R_{B_2} = (\frac{1}{2}, 0, \eta/4)a$

Te: $R_{C_1} = (u, \frac{1}{4}, \eta/8)a$ $R_{C_2} = (1 - u, \frac{3}{4}, \eta/8)a$ (1)

$R_{C_3} = (\frac{1}{4}, \frac{1}{2} + u, 3\eta/8)a$ $R_{C_4} = (\frac{3}{4}, \frac{1}{2} - u, 3\eta/8)a$

where $a = 6.3923$ Å (according to the virtual crystal approximation (VCA)) and $\eta = c/a = 2$ (assuming no tetragonal distortion), u is a dimensionless 'anion displacement parameter' which is related to the bond lengths according to the following expressions

$$R_{AC} = [u^2 + (4 + \eta^2)/64]^{1/2}a$$

$$R_{BC} = [(u - \frac{1}{2})^2 + (4 + \eta^2)/64]^{1/2}a$$ (2)

$$u = \frac{1}{4} + (R_{AC}^2 - R_{BC}^2)/a^2.$$

To keep the bond lengths in agreement with the experimental results [12], R_{AC}(Cd–Te) = 2.80 Å and R_{BC}(Mn–Te) = 2.75 Å, we have used $u = 0.257$ in our calculations.

The calculated band structure of CdMnTe$_2$ in this chalcopyrite structure is given in figure 3 from which we see that the lowest valence band in this system is constituted primarily from Te s orbitals (centred at −11.4 eV), with a minor Cd and Mn character. The next band is the Cd 4d band centred at $E_v - 8.8$ eV. The states between $E_v - 6.0$ eV ~ E_v form the p–d mixed valence band, while in the lower part of the band, the contributions are mainly from Mn(1) 3d↑ orbitals. In the states of the upper part of the band, the p–d mixtures are almost uniform contributions from the Te 5p orbitals (about 70%) and Mn(1) 3d↑ orbitals (20%). In the states near the valence band
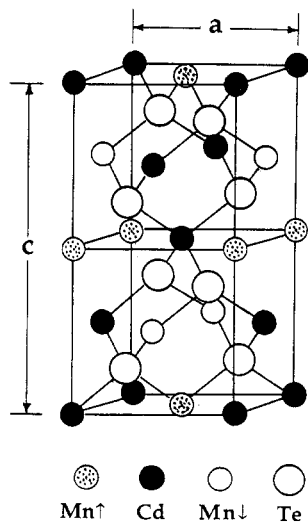
Mn↑ Cd Mn↓ Te

Figure 2. Chalcopyrite structure of CdMnTe$_2$.
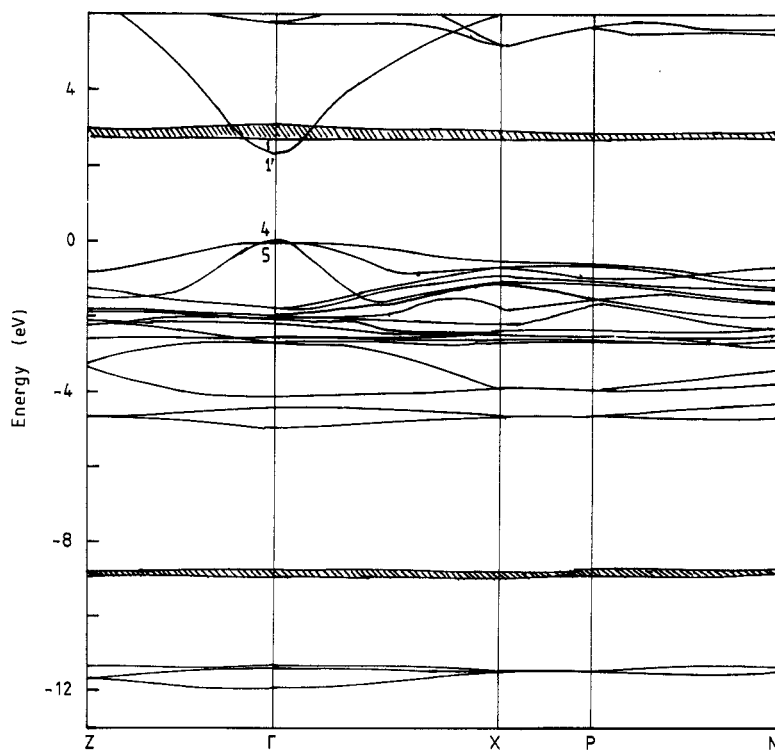
Figure 3. Electronic band structure of AF CdMnTe$_2$ in the chalcopyrite structure. The shaded areas denote the d electron bands.

maximum, i.e., Γ_4 and Γ_5, the d contributions are about 18%. This means that strong hybridisation occurs between the s–p bands and 3d orbitals. The energy gap in the calculated model is about 2.3 eV. The conduction band minimum (CBM) in figure 3 is of pure s character which is contributed from the Cd and Mn s orbitals and this s band is dispersed quickly from the Γ point. The shaded area is the contribution of Mn(2) 3d↓ orbitals. In our calculation, it shows a narrow band which corresponds to local orbitals of 3d↓ electrons. The splittings of the crystal field in the 3d↓ narrow band are too small and these may be due to the large separation between the 3d↓ orbital energy and the Te 5p orbital energy.

As seen from figure 3 and described in the prior section, the transition of an electron from the valence band maximum to the conduction band minimum is normally a p → s transition (E_0 transition). For a higher transition energy above E_0 we can conceive of a transition in which a valence band electron is added to the lowest unoccupied Mn orbital (a 'Te p → Mn d↓' transition). Because of the large mixing of the Te P and Mn d states at the VBM, this transition also has some d → d* character. Such p–d excitation in our calculation is about 2.6 eV. This transition energy is higher than the observed experimental data [15], the discrepancy being due to a too large parameter value of the 3d↓ orbital energy adopted in our calculation. In our case, we are aware of the tendency of the energy levels under hydrostatic pressure, the relative energy differences between different transitions can serve as a qualitative description of the physical origin.

Consider a ZB crystal and ignore for the moment the cation d states. The state near the band edge at Γ can be described qualitatively by a simple tight-binding model retaining the cation p orbitals (p^c with energy E_{pc}) and the anion p orbitals (p^a with energy E_{pa}). Since both have the same symmetry representation Γ_{15}, they can interact through a coupling matrix element V_{pp}, forming a lower energy bonding state at energy

$$E(\Gamma_{15v}(p)) = (E_{pc} + E_{pa})/2 - [(E_{pa} - E_{pc})^2/4 + V_{pp}^2]^{1/2} \qquad (3)$$

and an antibonding state at

$$E(\Gamma_{15c}(p)) = (E_{pc} + E_{pa})/2 + [(E_{pa} - E_{pc})^2/4 + V_{pp}^2]^{1/2}. \qquad (4)$$

The same expressions for the $\Gamma_{1c}(s)$ and $\Gamma_{1v}(s)$ states of the s orbitals are valid as above by changing E_{pa} to E_{sa}, E_{pc} to E_{sc}, and V_{pp} to V_{ss}. If, however, cation d states are included at an energy E_{dc}, they too have a representation of t_2 symmetry and can couple, through matrix elements V_{pd}. This coupling can lead to an inversion of the order of d orbitals ($\Gamma_{15}(d)$) relative to $\Gamma_{12}(d)$ and an upward shift of $\Gamma_{15}(pd)$ relative to the $\Gamma_{15}(p)$ state. The magnitude of the shift can be estimated as

$$\Delta E_{pd} \sim V_{pd}^2/(E_{pa} - E_{dc}). \qquad (5)$$

Estimating $V_{pd} = A r_d^{3/2}/d^{7/2}$, $V_{ss} = -5.28\hbar^2/(md^2)$, and $V_{pp} = 1.28\hbar^2/(md^2)$, where r_d and d are the d orbital radius and the average bond length, respectively, from Harrison's formulae [16], one may find the qualitative variations of the thresholds of the p → s and p → d transitions under the pressure exerted. It is obvious that $\Gamma_{15c}(s)$ (4) varies quickly upwards when the bond length d is reduced, while $\Gamma_{15v}(p)$ varies downwards (3). Therefore, for the normal p → s transition, the energy gap of the sp bond ZB structure increases with increasing pressure. The increased magnitude of the energy gap with pressure exerted can be reduced by taking into account the p–d repulsion (5) into the $\Gamma_{15}(p)$. The
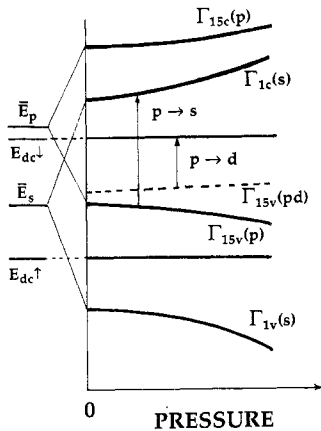
Figure 4. Schematic plot of the energy level inter-action scheme with increasing pressure in the T_d symmetry. $\bar{E}_s$ and $\bar{E}_p$ are the average s orbital and p orbital energies of anion and cation atoms, respectively. $E_{dc}\uparrow(\downarrow)$ represents the cation spin up(down) d orbital energy.
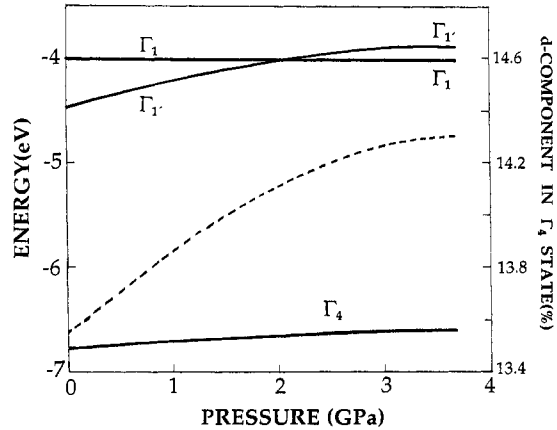
Figure 5. Calculated energy levels of $CdMnTe_2$ at the Γ-point (full curves) and the percentage d component at the Γ_4 state (broken curve) due to the p–d hybridisation with increasing pressure. Γ_4: the VBM; Γ_1: the CBM of the d character band; and Γ_1: the CBM of the s character band.

schematic picture is shown in figure 4. Keeping the matter in mind, we turn to see the effects of the AF ordering of Mn atoms on the electron band structure. As shown in figure 1, both spin-up and spin-down Mn 3d states are closer to the VBM in the AF phase, thus increasing the p–d hybridisation. If there is an equal number of Mn atoms with 3d levels below and above the Te p levels, the hybridisation results in an equal repulsion to the Te p band edge Γ_5 by $d\downarrow$ and $d\uparrow$, hence no pressure effects can be caused at Γ_5 by the Mn 3d electrons. However, $E_{d\downarrow} - E_p$ is not equal to $E_p - E_{d\uparrow}$ in general, so the p–d repulsion plays an important role at band edge Γ_5. This effect could also be significant in $CdMnTe_2$ because the Cd 4d electrons interact with the Γ_4 state, too (see figure 3). In this chalcopyrite structure, the Mn $d\downarrow$ band is located within the normal s–p band gap as that in AF MnTe and the bottom of the band is almost dispersionless. Therefore, in the p $\rightarrow$ d transition from VBM (Γ_4) to the $3d\downarrow$ band, the pressure dependence of the optical absorption edge is determined only by the variations of Γ_4 with pressure. In the strong p–d hybridisation case, Γ_4 could be repelled upwards in energy with increasing pressure and one may expect a negative pressure coefficient of the absorption edge. On the other hand, the energy in the CBM of the s states is shifted quickly upwards by increasing pressure, while still retaining an increasing p $\rightarrow$ s transition, but the magnitude of the increase is now less than that of the pure s–p band without the interaction of the d electrons.

Figure 5 shows the calculated results of the energy levels related to the absorption edge at the Γ-point under pressure. The pressure values are derived from the relation of the volume changes of the unit cell with respect to the experimental pressures [17]. The relative change of volume can be expressed by

$$V/V_0 = 1 + a_1 P + a_2 P^2 \tag{6}$$

where a_1 is the compressibility of the solid, and a_2 the second pressure coefficient. Taking $a_1 = -0.025$ GPa^{-1} and $a_2 = 0.0034$ GPa^{-2} from [17] in our calculations, we have fitted

the calculated energies in a simulation procedure. The first-order pressure coefficient of the p–d transition is -5.67×10^{-3} eV/10^8 Pa which agrees very well with the experimental data [10] -5.00×10^{-3} eV/10^8 Pa. For the normal s–p band gap $\Gamma_{1'}$–Γ_4, the calculated energy difference shifts to higher energy with increasing the pressure at a rate of 7.89×10^{-3} eV/10^8 Pa, which is in excellent agreement with the observed data [10] 8.0×10^{-3} eV/10^8 Pa for $Cd_{1-x}Mn_xTe$ with $x < 0.3$. The result means that the linear pressure dependence of the absorption edge at lower Mn-concentrations still holds for the p $\rightarrow$ s transitions at higher Mn-concentrations. Such a transition has been identified in photoluminescence experiments [4].

We have calculated the angular momentum decomposed charge in the eigenvalues at the Γ-point to investigate the p–d hybridisation at the band edge for $CdMnTe_2$. For the Γ_4 state, the percentage of the d character component with pressure are schematically shown in figure 5 by the broken curve. From this we can see that the d component increases with increasing pressure in the predominantly p character Γ_4 state. Though the magnitude of the increase is not so large, the effect of the d component on the optical absorption edge is significant as shown in figure 5 by the full curves. Our results also show that the p–d hybridisation is almost uniformly shared among the Te 5p valence bands which implies that the 3d↑ orbitals are not highly localised but are broadened; this conclusion is in agreement with recent photoemission experiments [18].

We would like to discuss the validity of the chalcopyrite structure $CdMnTe_2$ as a model for an ordered, 50% ~ 50% alloy of $Cd_{1-x}Mn_xTe$. Phase diagram calculations [19] for bulk and epitaxial $A_xB_{1-x}C$ alloys have shown that ordering of the $A_nB_{4-n}C_4$ ($1 \leqslant n \leqslant 3$) compound can occur at the stoichiometric composition $X_n = n/4 = \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$, below some critical temperature. A total energy calculation [12] indicated that at low temperature and slow growth rates, the $x = \frac{1}{2}$ alloy might produce a crystallographically ordered, stable $CdMnTe_2$ compound. Denoting $P_n(x)$ as the probability of finding cluster n (of $A_nB_{4-n}C_4$) at composition x, we will approximate

$$P_n(x) = \binom{4}{n}x^n(1-x)^{4-n} \tag{7}$$

and the band energy $E_k(x)$ of the alloy can be obtained from [20]

$$E_k(x) = \sum_{n=0}^{4} P_n(x)E^n(k) \tag{8}$$

where $E^n(k)$ is the band energy for crystals formed from the different nearest-neighbour configurations that can occur in alloys. Theoretical research [20] showed that the alloy band structure calculated according to (8) is in good agreement with experiment with regards to the valence bands and band gap bowing than that of usual treatments of alloys using the VCA and coherent potential approximation (CPA) [20]. As seen from (7), the $n = 2$ ordered structure possesses the largest probability at $x = \frac{1}{2}$. The chalcopyrite structure is one of the most probable ordered models of $n = 2$ type. Considering the fact [3] that the well-defined different nearest-neighbour Cd–Te and Mn–Te distances (a 'bimodel' distribution) exist in $Cd_{1-x}Mn_xTe$, the local bonding observed in $Cd_{1-x}Mn_xTe$ [3] is similar to that found in the chalcopyrite structure. In addition, the antiferromagnetic coupling between nearest neighbours over Mn sites only can be presented apparently in our model as to simulate the properties of the suggested AF ordered phase at high x-concentration [1]. We therefore believe that the electronic structure calculated for the probable chalcopyrite structure could reflect the main features of that of the

$Cd_{0.5}Mn_{0.5}Te$ alloy though we did not calculate the weighted averages of the band structures with different configurations n in (8). Such a chalcopyrite analogue had also been used to assist in the modelling of the random ZB solid solution in the alloys of $Ga_{1-x}In_xAs$ [21], $Al_xGa_{1-x}As$ and $GaAs_xSb_{1-x}$ [22].

The present study of the pressure dependence of the absorption edge at $x = 0.5$ in $Cd_{1-x}Mn_xTe$ might assist in the understanding of the concentration-independence behaviour of the absorption edge. At high x-composition, the negative pressure coefficient is determined by $\Gamma_{15v}(pd)$, which is closely related to the competition of the energy shifts between the upward ΔE_{pd} (5) and downward $\Gamma_{15v}(p)$ (3) as illustrated in figure 4. As seen in figure 3, the CBM of the s orbital energy $\Gamma_{1c}(s)$ is very close to the bottom of the Mn $3d\downarrow$ band, the s character CBM could shift upwards into the $3d\downarrow$ band while the Mn composition increased and the resultant absorption edge is determined by the transition from VBM to the bottom of the $3d\downarrow$ band. Since the bottom of the $3d\downarrow$ band is almost unchanged, the change of the absorption edge is governed by that of the $\Gamma_{15v}(pd)$. The effect on the absorption edge with increasing Mn composition is equivalent to applying pressure to the alloy at a fixed value of x. The anomaly in the absorption edge occurs at large Mn-composition with x ranged between 0.5 to 0.7, the change of $\Gamma_{15v}(pd)$ with composition is too small to measure [23] in comparison to that of $\Gamma_{1c}(s)$. This might possibly be the reason why the absorption edge is almost concentration independent at large Mn-composition as found in [8]. However, at higher Mn-composition, the quick increase in ΔE_{pd} with increasing pressure would result in a quick upward shift in $\Gamma_{15v}(pd)$ as compared with that of the lower composition, and then a lower absorption edge and a larger negative pressure coefficient should be expected with increasing the composition under pressure. The measured absorption edge of $x = 0.675$ which is lower than that of $x = 0.5$ (whereas the value of the negative pressure coefficient of $x = 0.675$ is larger under the same pressure [10]) can be reasonably attributed to the same origin as explained above.

It has generally been recognised that the negative pressure coefficient of the optical absorption edge for $Cd_{1-x}Mn_xTe$ with $x > 0.5$ is associated with the presence of the Mn^{2+} $3d^5$ states, that is the $^6A_1 \rightarrow {}^4T_1$ transition within Mn^{2+} 3d levels, which makes the absorption edge pinning greater with further increase of x [6]. One could estimate the pressure coefficient for this transition by crystal field considerations [6, 24]. Unfortunately, the calculated value is about -2×10^{-3} eV/10^8 Pa, which is much smaller than the observed one [10]. As stressed above, the top of the valence Te 5p band is strongly hybridised with the Mn 3d electrons, if the observed absorption edge is dominated by the transition from VBM to the empty Mn $3d\downarrow$ band, it can have a quite different pressure coefficient from the transition within $3d^5$ levels. In our model of $Cd_{0.5}Mn_{0.5}Te$, i.e. the chalcopyrite structure $CdMnTe_2$, the excellent agreement of the $p \rightarrow d$ pressure coefficient -5.67×10^{-3} eV/10^8 Pa with experimental data [10] of -5.0×10^{-3} eV/10^8 Pa, and of the $p \rightarrow s$ 7.89×10^{-3} eV/10^8 Pa with experimental data [4] 8.0×10^{-3} eV/10^8 Pa, vindicated the approach of our model to the alloy $Cd_{1-x}Mn_xTe$. From our calculations, we can attribute the observed optical absorption edge anomaly for $Cd_{1-x}Mn_xTe$ with $x > 0.5$ to the transition from VBM to the $3d\downarrow$ levels, the origin of the decrease in the 'p–d' transition is due to the VBM upward shift in energy (by increasing the p–d coupling) while the bottom of the empty $3d\downarrow$ bands remain unchanged.

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