

Crystal Lattice Distortion of CdTe Matrix by Introducing Zn and Mn Atoms

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Abstract: A theoretical investigation of the crystal lattice of compounds CdTe and MnTe belonging to the II-VI family when they are alloyed by introducing Zn and Mn atoms, respectively, has been performed. For this purpose the tetrahedral model has been chosen in order to calculate the energy of deformation and the bond lengths. The model considers that: the microscopic structure is zinc blend. The chemically ordered sublattice is deformed. The chemically disordered sublattice is undeformed. $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ form the zinc blend structure until $x = 0.70$. The obtained results for $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ show that there is no angle tilt due to the alloying phenomenon, which is confirmed otherwise by the experiments. The application of the model to $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ until $x = 0.70$ showed the same results.

Key words: $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, energy of deformation, tetrahedral model, bond length, angle tilt

INTRODUCTION

CdTe is a semiconductor material belonging to the II-VI family. It is one of the materials which have received a great interest because of their intrinsic properties, such as, for CdTe, its wide gap (1.51 eV at room temperature), which permit to it the IR, X and γ detection (Prias-Barragan *et al.*, 2006) and its very important luminescence efficiency.

In addition the use of CdTe becomes more important when we introduce a certain quantity of Zn atoms, which permit to have a very effective material in the medical imagery and in the infrared detection and also used as substrate for the molecular beam epitaxy (Tseng *et al.*, 2003).

The $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ crystal is considered in many studies as a competitive material of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ in the X-ray and γ -ray detector applications (Zhang *et al.*, 2007), with several advantages such, its segregation coefficient close to unit (Triboulet *et al.*, 1990).

The previous studies focused on two aspects:

The theoretical aspect, which considers on one hand, the average distribution given, generally, by the VCA (Virtual crystal approximation) model (Wu *et al.*, 1993) and the Pauling model and on the other hand, the minimum energy of the deformation connected to the concentration and which can be found otherwise in Keating's (1996) works. The experimental aspect can't, on one hand, describe the deformation shape and on the other hand confirms that the VCA and Pauling models are not valid.

In addition all authors who used the energy in their studies consider that deformation is made without angle tilt, however they don't give any reasons.

This study is a contribution in this field; we have carried out an investigation in the knowledge of the locale deformation of the CdTe matrix when Zn and Mn atoms are introduced. This knowledge is greatly required in many applications, such as detection or manufacture of special devices, which are closely related to the local state.

Further more the growth method is also connected to the local state especially for CdMnTe and finally there are some differences between the properties of the matrix and the alloys.

To reach this aim we calculate the deformation energy and the bond lengths, considering or not the angle tilt.

Some considerations were taken into account: the theoretical basis, the description of the chosen model, the deformation energy and the bond lengths calculation considering or not angle tilt, followed by a discussion and ended by a conclusion summarizing the main results.

THEORETICAL BASIS

The mixture of ZnTe and CdTe permits to obtain solid solutions $\text{A}_{1-x}\text{B}_x\text{C}$ for all concentrations ($0 \leq x \leq 1$). These ternary alloys have a zinc blend structure, where the lattice parameter varies according Vegard's law (Motta *et al.*, 1985). The same behavior affect CdTe mixed with MnTe.

We are going now to apply the model to $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, which will be the same for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$.

The tetrahedral model: Several models have been proposed (Harrison, 1999; Rabouch *et al.*, 2002) to explain experimental results of crystalline deformation. among these models we have chosen a structural model, named “tetrahedral model” (Motta *et al.*, 1985), which we applied to our special case. It is based on the following considerations:

- The sublattice Cd (Zn or Mn) chemically disordered was considered as being non-deformed and the one (Te) chemically ordered as deformed.
- A used tetrahedron which is considered as unit cell, contain four atoms (Cd) at the summits bounded to one anion (Te). The tetrahedral can possess five configurations as mentioned in several papers (Motta *et al.*, 1985).
- Because of the covalent character the interaction between tetrahedrons was neglected. Thus only the second neighbors were been considered.

The energy deformation: An approximation based on the VFF (Valence Force Field), (Martin, 1970), suggested by Keating (1996) and giving the energy of deformation and showed by the following equation has been used:

$$U = \frac{1}{2} \sum_{i=1}^4 \frac{3}{4} \alpha_i \frac{\left[\Delta \left(\vec{d}_i^1 \cdot \vec{d}_i^1 \right) \right]^2}{\left(d_i^0 \right)^2} + \frac{1}{2} \sum_{s=1}^2 \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{3}{4} \beta_{ij} \frac{\left[\Delta \left(\vec{d}_i^s \cdot \vec{d}_j^s \right) \right]^2}{d_i^0 \cdot d_j^0} \quad (1)$$

Where, $s = 1, 2$ indicates atom of group II and VI in the unit cell I. The bonds related to each atom are indexed by i and j .

$$\vec{d}_i^s \text{ and } \vec{d}_j^s$$

represent the bond vectors which connect the atom s to its near neighbors, d_i^0 is the bond length i in the pure state.

α_i and β_i are, respectively the bond stretching force constant of the bond i and the bond-bending one between the bond i and the bond j .

In the case, where we take the angles constant and equal to 109.47° (Keating, 1966), the Eq. (1) becomes:

$$U = \frac{1}{2} \sum_{i=1}^4 \frac{3}{4} \alpha_i \frac{\left[\Delta \left(\left(\vec{d}_i^1 \right)^2 - \left(d_i^0 \right)^2 \right) \right]^2}{\left(d_i^0 \right)^2} + \frac{1}{2} \sum_{s=1}^2 \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{3}{12} \beta_{ij} \frac{\left[\left(d_i^0 \right)^2 - \left(d_i^s \cdot d_j^s \right) \right]^2}{d_i^0 \cdot d_j^0} \quad (2)$$

For our alloy $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, we use the following constants α_{CdTe} , β_{CdTe} (d_{CdTe}^0) for the bonds Cd-Te and the angles Cd-Te-Cd and Te-Cd-Te, the constants α_{ZnTe} , β_{ZnTe} (d_{ZnTe}^0) for the bonds Zn-Te and the angles Zn-Te-Zn and Te-Zn-Te and the constants

$$\sqrt{\alpha_{\text{ZnTe}} \alpha_{\text{CdTe}}}, \sqrt{\beta_{\text{ZnTe}} \beta_{\text{CdTe}}}, d_{\text{ZnTe}}^0, d_{\text{CdTe}}^0$$

for the angles Cd-Te-Zn, Te-Cd-Zn and Te-Zn-Cd.

Energy of deformation when neglecting the angle tilt:

The energy of deformation is considered as the difference occurred after an only lengthened or compressed bond length. The calculation concept is based on the fact that the unit cell is a perfect tetrahedron, which has (n) Zn-Te (Zn (x)) bonds and $(4-n)$ Cd-Te (Yn (x)) ones. So the equation of the deformation energy becomes:

$$E_n(x) = \frac{3}{8} (4-n) \alpha_{\text{CdTe}} \frac{\left(Y_n^2(x) - R_{\text{CdTe}}^2 \right)^2}{R_{\text{CdTe}}^2} + \frac{3}{8} (n) \alpha_{\text{ZnTe}} \frac{\left(Z_n^2(x) - R_{\text{ZnTe}}^2 \right)^2}{R_{\text{ZnTe}}^2} \quad (3)$$

Energy of deformation when introducing the angles tilt:

In addition to the bond length deformation, the tilt of the angles around the position of the two atoms of the four near neighbor tetrahedrons of the unit cell were, for this time, taken into account (Fig. 1). The total deformation energy becomes:

$$U_n(x) = \frac{1}{8} \left\{ \beta_{\text{CdTe}} \left[n \left(\frac{n}{2} - 5 \right) \right] + 3(4-n) \alpha_{\text{CdTe}} \right\} \frac{\left(Y_n^2(x) - R_{\text{CdTe}}^2 \right)^2}{R_{\text{CdTe}}^2} + \frac{1}{8} \left\{ 3n \alpha_{\text{ZnTe}} + \beta_{\text{ZnTe}} n \left(\frac{n}{2} + 1 \right) \right\} \frac{\left(Z_n^2(x) - R_{\text{ZnTe}}^2 \right)^2}{R_{\text{ZnTe}}^2} + \frac{1}{8} n(4-n) \frac{\sqrt{\beta_{\text{CdTe}} \beta_{\text{ZnTe}}}}{R_{\text{CdTe}} R_{\text{ZnTe}}} \left[R_{\text{CdTe}} R_{\text{ZnTe}} - Y_n(x) Z_n(x) \right]^2 \quad (4)$$

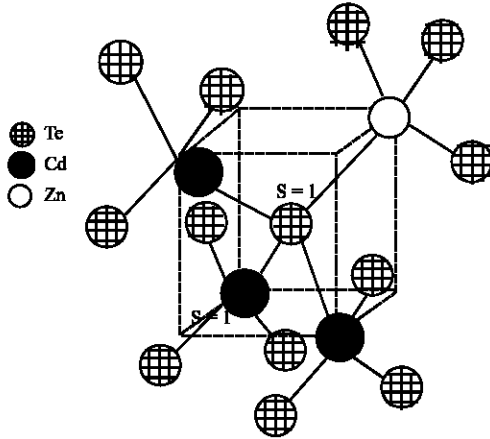


Fig. 1: Unit cell of Cd1-xZnxTe with n = 1

The bond lengths: As first assumption, we consider the tetrahedron unit cell as perfect. Its dimensions are determined by the lattice parameter $a(x)$. This leads, easily, to have relations between $Y_n(x)$ and $Z_n(x)$ as follows:

$$Y_0(x) = a(x)\sqrt{3}/4 = Z_4(x) \quad (5a)$$

$$Y_1(x) = \left[\frac{a^2(x)}{2} + Z_1^2(x) - \frac{2}{\sqrt{3}} a(x) \cdot Z_1(x) \right]^{1/2} \quad (5b)$$

$$Y_2(x) = \left[\frac{a^2(x)}{4} - a(x) \left(Z_1^2(x) - \frac{a^2(x)}{8} \right)^{1/2} + Z_2^2(x) \right]^{1/2} \quad (5c)$$

$$Y_3(x) = \frac{a(x)}{\sqrt{3}} - \frac{1}{2} \left[4Z_3^2(x) - \frac{2}{3} a^2(x) \right]^{1/2} \quad (5d)$$

Each concentration x gives one or more configurations and then several values of each bond type. To calculate the average of bond lengths related to a concentration x , the distribution probability of each tetrahedron was used. This is given by the Eq. (6) and the bond lengths $Y(x)$ and $Z(x)$ are illustrated by the Eq (7).

$$P(n, x) = \binom{4}{n} x^n (1-x)^{4-n}, \quad \binom{4}{n} = C_4^n = \frac{4!}{(4-n)!n!} \quad (6)$$

$$y(x) = \frac{\sum_{n=0}^4 (4-n) p_n(x) y_n(x)}{\sum_{n=0}^4 (4-n) p_n(x)}, \quad Z(x) = \frac{\sum_{n=0}^4 n p_n(x) Z_n(x)}{\sum_{n=0}^4 n p_n(x)} \quad (7)$$

Introducing the (5 a, b, c, d) relations into the energy equation, the formula can be reduced to an equation with one variable, which, after minimizing, permits to calculate the minimum of the deformation energy and the bond lengths at the equilibrium.

A numerical method was used to calculate different parameters because the analytical approach is very complex.

For concentrations $x = 0$ and $x = 1$, giving, respectively, pure materials CdTe and ZnTe, the bond lengths are giving by:

$$Y_0(x) = R_{CdTe} = a_{CdTe} \sqrt{3}/4$$

$$Z_0(x) = R_{ZnTe} = a_{ZnTe} \sqrt{3}/4$$

RESULTS AND DISCUSSION

The calculation of the deformation energy has allowed us to:

- Clarify the behavior of the CdTe matrix when this material is deformed by introducing Zn atoms.
- Know the variation of the energy as a function of the concentration x for each tetrahedron (n), which the minimum energy was obtained for a well-known concentration (Fig. 2).
- Compare the obtained results, considering or not angles tilt.
- Conclude that the deformation of the CdTe matrix at the atomic scale is made without angles variation.

The Fig. 3a and b show that the bond lengths variation Cd-Te and Zn-Te diminish linearly as a function of the concentration x and thus confirm that the angle tilt has no effect on the deformation.

The Fig. 4a and b show the comparison between our theoretical curves and experimental ones (EXAFS) (Koteski *et al.*, 2004). It is clear that the used model can explain, exactly, what that was occurs after deformation.

The good agreement between theoretical and experimental results obtained with Zn impurities introduced in CdTe matrix has encouraged us to apply the

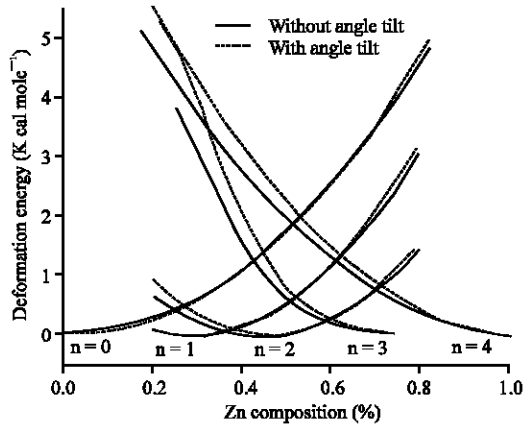


Fig. 2: Comparison between the deformation energy of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ calculated with or without angle tilt

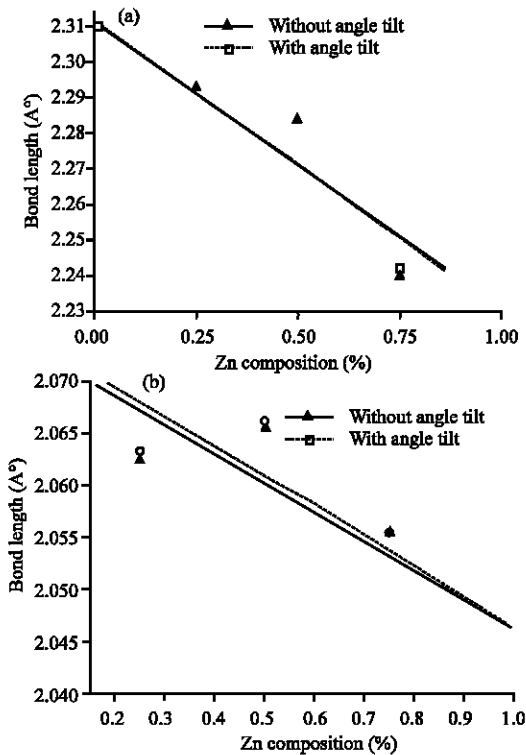


Fig. 3: Comparison between the bond lengths Cd-Te and Zn-Te calculated with or without angle tilt

used model to other alloys. The only two conditions required are: having zinc blend structure and a variation of the lattice parameter following the Vegard's law. The results of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ are shown in Fig. 5-7

For this alloy, we have to consider that we have a solid solution up to the concentration $x = 70\%$, which oblige us to stop our calculation at this concentration, the model being not valid beyond.

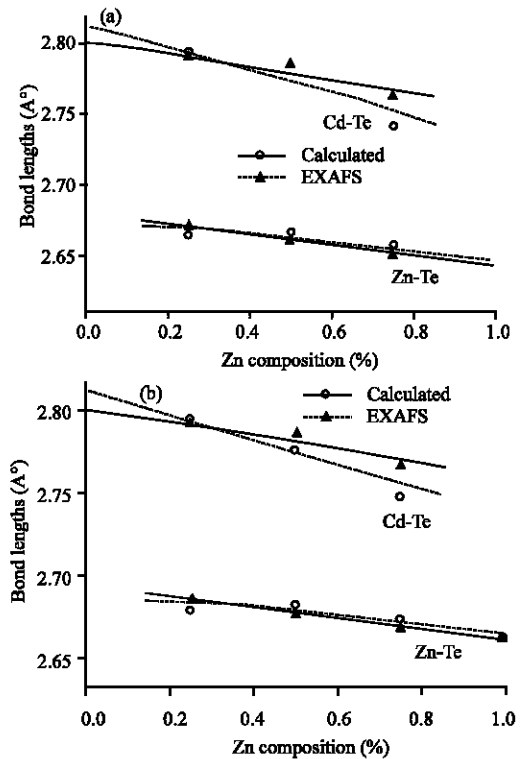


Fig. 4: Comparison between the bond lengths calculated with (a) and without (b) angle tilt and EXAFS results for $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ alloys

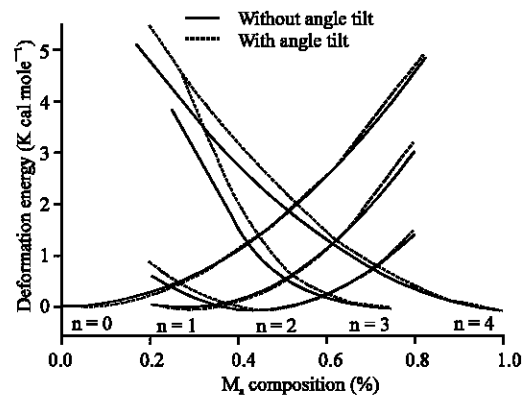


Fig. 5: Comparison between the deformation energy of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ calculated with or without angle tilt

The obtained results (Fig. 5-7) confirm once again the good choice of the used model.

The deformation state of this alloy is well described through different curves drawn in the concentration domain $[0-0.70]\%$.

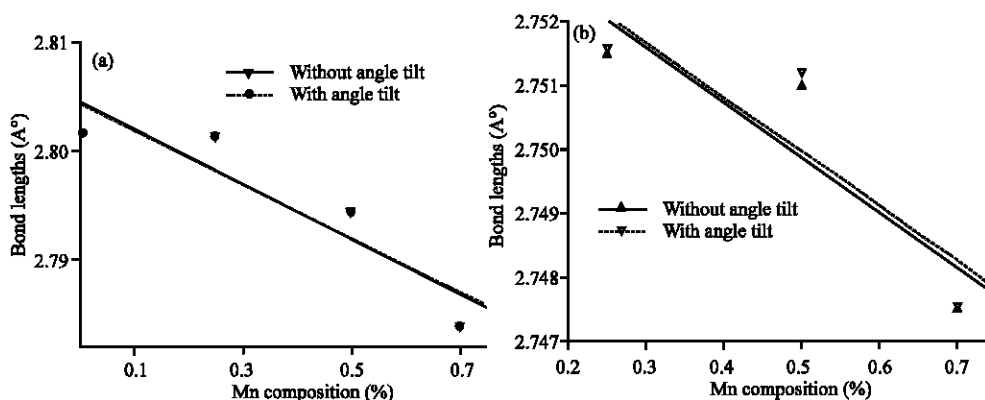


Fig. 6: Comparison between the bond lengths Cd-Te (a) and Mn-Te (b) calculated with or without angle tilt

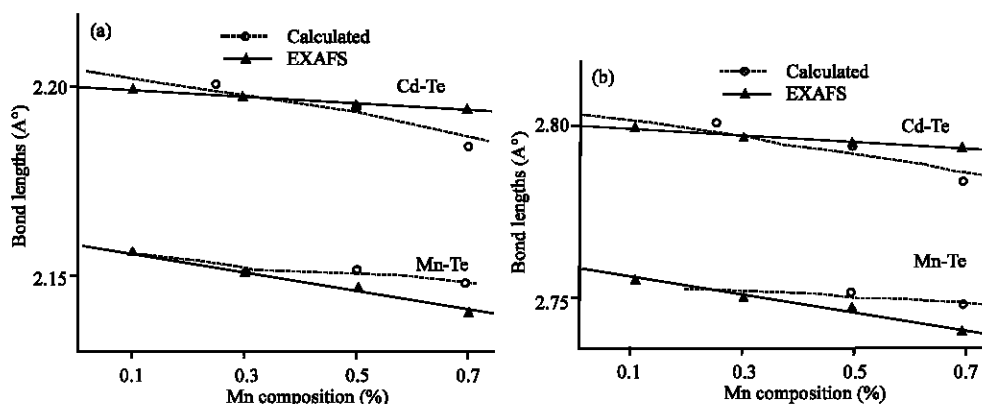


Fig. 7: Comparison between the bond lengths calculated with (a) and without (b) angle tilt and EXAFS results for $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$

CONCLUSION

This research represents a contribution in the investigation of the deformation energy and the bond lengths of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ alloys as a basic material.

To realize this study a numerical calculation method based on 2 informatic programs has been used.

The results carried out for $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ were very satisfactory, we have been encouraged to apply the model to $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, which compete with $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ in several properties.

The obtained results are summarized as follows:

- The calculation of the deformation energy leads to locate the energy minimum and then permits to precise the most probable corresponding configuration.
- The difference between the two kind curves, of the energy or the bond lengths, obtained considering or not angle tilt is very weak for $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$.

- The bond calculation showed, as for the energy, a weak difference between the curves, considering or not the angle tilt, for the two materials, which means that the deformation is made without angle tilt.
- The comparison with the experiment permit us to conclude that the used model gives an important precision and allows us, as a consequence, to describe correctly the local deformation.

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