Chapter 6

Structural, Elastic, Mechanical and Anharmonic Properties of II-VI and III -V Diluted Magnetic Semiconductors

6.1 Introduction

Diluted magnetic semiconductors (DMS's) due to their unique characteristics have become important materials in the field of opto electronic devices such as solar cells, IR detectors, magnetic field sensors, and optical isolators [1]. Recently many investigations are focused on the application of the concept of spintronics or magneto electronics in DMS's, because they provide testing ground for spintronics due to their simple band structures and excellent magneto optical and transport properties [2]. Group III-V and II-VI ferromagnetic diluted magnetic semiconductors are important materials for the applications of spintronics due to their good compatibilities with existing semiconductor devices [3].

Zinc-blende II-VI semiconductors offer a lot of interesting opportunities for the investigations of various physical properties. This is due to the large span of energy gaps characterizing them as well as the facility of the growth of II-VI ternary alloys over a significant composition range. Replacement of the group II element by 3d transition metal ion enables one to obtain a semi magnetic (diluted magnetic) semiconductor which have been the subject of different studies due to their interesting electrical [4], magnetic [4], optical [4,5], elastic [6], phonon properties [7-10] and the pressure induced phase transition [7-11].

ZnSe based ternary compound semiconductors, which are random mixtures of ZnSe and magnetic or nonmagnetic ions, have attracted much attention in recent years due to the study of the basic physical properties such as the variation of long wave length optical phonon vibration modes versus the mole fraction of nonmagnetic ions and its ability to tune the band gap and lattice constant for the application in optoelectronic devices. The diluted magnetic semiconductors (DMS) $Zn_{1-x}M_xSe$ (M=Cd, Fe and Mn), one of the ZnSe ternary compound semiconductors, have been reported to have many interesting physical properties [1, 4-19]. In recent years, due to the progress in the diamond anvil technique some important results of the pressure induced phase transition of ZnSe ternary compound semiconductors containing magnetic ions have been obtained by using energy dispersive x-ray diffraction (EDXD) [12] and Raman spectroscopy [6-9]. It was found that the existence of magnetic ions in the ZnSe crystal resulted in a reduction of the transition pressure. Recently, a systematic investigation by using EDXD on ZnSe ternary compound semiconductors containing magnetic as well as nonmagnetic ions, $Zn_{1-x}M_xSe$; (M=Cd, Fe and Mn) has been performed by Lin et al [20].They observed that these compounds go to the NaCl (B1) structure from its original Zinc blende (B3) structure at about 11.4, 9.5 and 9.6 GPa for $Zn_{0.84}Fe_{0.16}Se$, $Zn_{0.9}Cd_{0.1}Se$ and $Zn_{0.76}Mn_{0.24}Se$ respectively which is about 3-5 GPa less in comparison to the ZnSe compound semiconductor.

In the recent time great efforts have been made in Mn-doped III-V DMS's such as $Ga_{1-x}Mn_xAs$ and $In_{1-x}Mn_xAs$ due to ferromagnetic long range ordering caused by the carrier mediated ferromagnetic interaction between the localized d spins of Mn ions [21]. The Mn^{+2} ion doped DMS's $Ga_{1-x}Mn_xAs$ have highest Curie temperature as high as 110 K [24]. Recently ferromagnetic II-VI DMS's have also been observed in heavily p-doped $Zn_{1-x}Cr_xTe$ and $Be_{1-x}Mn_xTe$, but with lower Tc (~2-3 K) [22]. The doping inevitably changes both conductive and optical properties, and to control both independently it is desired to obtain ferromagnetic DMS. Thus ferromagnetic II-VI DMS's are very promising materials for device applications.

Cr doped DMS's are crucial due to their d-d super exchange interaction which predicts ferromagnetism within it [23]. Satio et al [24] and Okazawa et al [25] observed this ferromagnetic d–d exchange in $Ga_{1-x}Cr_xAs$ epitaxial films. It has been theoretically proved that this ferromagnetic state is more stable than that in nonmagnetic state in Cr doped II-VI DMS [26]. An exchange interaction between p-holes and d spin of Cr ions has been reported in Cr doped II-VI DMS's such as $Zn_{1-x}Cr_xTe$ [27]. Recently Saito et al [28] have reported a ferromagnetic hysteresis loop in magnetization curve of an epitaxial film of $Zn_{1-x}Cr_xTe$ (x=0.035) and a quite high transition temperature of around 300 K [29]. Looking to the importance of Cr doped ZnTe II-VI DMS's; it is a right juncture to investigate the physical properties of this compound.

Looking to its academic and technological importance, we thought it pertinent to analyze the phase transition and anharmonic properties of $Zn_{1-x}M_xSe$ (with x=0.16, 0.10 and 0.24 for M = Fe, Cd and Mn respectively) and mechanical, elastic and anharmonic properties of $Zn_{1-x}Cr_xTe$ diluted magnetic semiconductors. This analysis includes the description of high pressure behaviour such as equation of states, phase transition pressure for $Zn_{1-x}M_xSe$, third order elastic constants (TOEC) and pressure derivatives of the second order elastic constants (SOEC) and stability criterion for $Zn_{1-x}M_xSe$ and $Zn_{1-x}Cr_xTe$. For this purpose, we have employed a theoretical approach for the first time in the frame work of interionic potential approach based on the charge transfer effect arising from the deformation of the electronic shell due to overlap of neighboring ions. This effect is prominent under pressure and has been introduced phenomenologically in the potential and considered as a model parameter. This approach has been quite successfully used for the explanation of static, dynamical and high pressure behaviour of several compounds including zinc blende compound semiconductors [30-31] and DMS [32].

6.2 Theoretical Consideration

The details of the above mentioned many body interaction potential arising due to charge transfer and method of calculation adopted in the present paper are presented elsewhere [30-31,33]. Here, we briefly outline some of the useful features of the interaction potential. The potential energy framework of the body interaction potential mentioned above is expressed as [31].

$$U(r) = \sum_{i,j}{}' \frac{z_i z_j e^2}{r_{ij}} + \sum_{i,j,k}{}' \frac{z_i z_j e^2 f(r_{ik})}{r_{ij}} + \sum_{i,j}{}' b\beta_{ij} \exp\left[\frac{(r_i + r_j - r_{ij})}{\rho_{ij}}\right] \qquad (1)$$

which includes long range Coulomb (first term), three body interaction arising from the charge transfer effects (second term) commonly known as three body interaction (TBI), and Hartree Fock form of the short range repulsive energies (last term). This potential has three parameters b, ρ and f(r) known as hardness, strength, and TBI parameters respectively. For the simplicity only single ρ has been used. The TBI parameter f(r) has the functional form $f(r) = f_o \exp(-r_{ij}/\rho)$ and is considered to be effective upto the first neighbor only. The higher order derivatives of f(r) can be evaluated by assuming the above functional form. Moreover, this parameter has been considered structure dependent. The TBI or charge transfer parameter f(r) has been obtained from overlap integrals [33-34]. The remaining parameter b and ρ have been obtained by using the expression for bulk modulus and equilibrium condition [34-35]. The values of parameters obtained so have been presented in Tables 1 and 2. Using interionic potential given in equation (1) the expressions for SOEC, the pressure derivatives of second order elastic constants and third order elastic constants can be derived and found in ref. [36].

Thermodynamically, a phase transition is said to occur when changes in the structural details of the phase are caused by a variation of the free energy. The $Zn_{1-x} M_x Se$ compounds transform from their initial B3 (Zinc blende) to B1 (Rock salt) structure under pressure. The stability of a particular structure is decided by the minima of the Gibbs energy, which is given as

$$G = U + PV - TS \qquad (2)$$

Where U is the internal energy at 0 K, S is the vibrational entropy at absolute T, pressure P_t and volume V.

The Gibbs free energies $G_{B3}(r) = U_{B3}(r) + 3.08Pr^3$ for B3 phase and $G_{B1}(r') = U_{B1}(r') + (2.0) Pr'^3$ for B1 phase become equal at the phase transition pressure P and temperature 0K, i.e. ΔG ($=G_{B3} - G_{B1}$) becomes zero. Here the abbreviations U_{B3} and U_{B1} represent cohesive energies for the phases B3 and B1, respectively, and are written as,

$U_{B3}(r) = -1.638\, e^2\, Ze^2\, (Z+4f(r))/r + 4V_{ij}\,(r) + 6V_{ii}\,(r) + 6V_{jj}\,(r)$ (3) and

$U_{B1}\,(r\,') = -1.74756\, e^2\, Ze^2\, (Z+4f\,(r\,'))/r\,' + 6V_{ij}\,(r\,') + 6V_{ii}\,(r\,') + 6V_{jj}\,(r\,')$ (4)

Here r and r ′ are nearest – neighbor (nn) separations corresponding to Zinc blende and rocksalt phases, respectively.

Table 1: Input data from ref. [20] and Model parameters for $Zn_{1-x}M_xSe$ DMS.

Solids	**Input data**		**Model Parameters**		
	a (Å)	B(GPa)	b (x 10^{-19}J)	ρ (Å)	f (r)
$Zn_{0.76}Mn_{0.24}Se$	5.7080	0.6048	2.5944	0.421	-0.068
$Zn_{0.84}Fe_{0.16}Se$	5.8188	0.5885	2.56239	0.439	-0.066
$Zn_{0.9}Cd_{0.1}Se$	5.8254	0.6023	2.47062	0.431	-0.066

Table 2: Input data and Model Parameter for $Zn_{1-x}Cr_xTe$ ($0 \leq x \leq 1$).

Concentration	**Input parameter**					**Model Parameter**		
	r_+ (Å)	r_- (Å)	R (Å)	B_T (10^{11} dyne/cm^2)	a (Å)	b (10^{-19} J)	ρ (Å)	f(r)
ZnTe	0.74	2.11	3.050	5.28^a 5.28^b 5.08^c	6.100 6.100^a	2.713	0.41	-0.07318
$Zn_{0.8}Cr_{0.2}Te$	0.77	2.11	3.069	5.14	6.138	2.619	0.413	-0.07310
$Zn_{0.6}Cr_{0.4}Te$	0.80	2.11	3.088	5.00	6.176	2.472	0.422	-0.07190
$Zn_{0.4}Cr_{0.6}Te$	0.83	2.11	3.107	4.86	6.215	2.451	0.424	-0.07285
$Zn_{0.2}Cr_{0.8}Te$	0.86	2.11	3.127	4.70	6.254	2.382	0.426	-0.07243
CrTe	0.89	2.11	3.146	4.59^a 4.59^d	6.292^a 6.29^d	2.299	0.428	-0.07248

[a] From Our Present Calculation.
[b] From Ref. 35.
[c] From Ref. 42.
[d] From Ref. 39.

The short-range potentials for both the phases between the ions are written as

$$V_{ij}(r) = \sum_{i,j}{}' b\beta_{ij} \exp\left[\frac{(r_i + r_j - r_{ij})}{\rho_{ij}}\right] \tag{5}$$

where β_{ij} and ρ_{ij} are short-range parameters. For predicting the transition pressure, we have minimized the Gibbs free energies with respect to the interionic separations and calculated ΔG ($=G_{B3} - G_{B1}$) for various pressures.

The study of elastic constants (C_{11}, C_{12} and C_{44}) and their pressure derivatives at 0 K is relevant for understanding the nature of interatomic forces in them. Since these elastic constants are functions of the first and second order derivatives of the short range potentials, their calculation will provide a further check on the accuracy of short range forces in these materials. We shall use the following second order elastic constants (SOEC) as earlier derived ,

$$C_{11} = L\left[0.2477Z^2 + \frac{1}{3}(A_1 + 2B_1) + \frac{1}{2}(A_2 + 2B_2)\right], \tag{6}$$

$$C_{12} = L\left[-2.6458Z^2 + \frac{1}{3}(A_1 - 4B_1) + \frac{1}{4}(A_2 - 5B_2)\right], \tag{7}$$

$$C_{44} = L\left[-0.123Z^2 + \frac{1}{3}(A_1 + 2B_1) + \frac{1}{4}(A_2 + 3B_2) - \frac{1}{3}\nabla\left(-7.53912Z^2 + A_1 - B_1\right)\right] \tag{8}$$

Henceforth, the expressions for pressure derivatives of SOEC follow

$$3\Omega\frac{dB_T}{dp} = -\left[20.1788Z^2 - 3(A_1 + A_2) + 4(B_1 + B_2) + 3(C_1 + C_2)\right] \tag{9}$$

$$2\Omega\frac{d\sigma}{dp} = -\left[-11.5756Z^2 + 2(A_1 - 2B_1) + \frac{2}{3}A_2 - \frac{7}{2}B_2 + \frac{1}{4}C_2\right], \tag{10}$$

and

$$\Omega\frac{dC_{44}}{dp} = -\left\{\begin{array}{l} \left[0.4952Z^2 + \frac{1}{3}(A_1 - 4B_1 + C_1) + \frac{1}{4}(2A_2 - 6B_2 - C_2)\right] \\ + \nabla\left[-17.5913Z^2 + \left(A_1 - B_1 - \frac{2}{3}C_1\right)\right] \\ \qquad + \nabla^2\left[3.1416Z^2 + \frac{2}{3}(A_1 - B_1) + \frac{C_1}{3}\right] \end{array}\right\} \tag{11}$$

Furthermore, the expression for anharmonic third order elastic constant (TOEC), using the crystal potential given by equation (1) and the method of homogeneous deformation leads to the following expressions:

$$C_{111}=L\left[0.5184Z^2+\frac{1}{9}(C_1-6B_1-3A_1)+\frac{1}{4}(C_2-B_2-3A_2)-2(B_1+B_2)\right] \tag{12}$$

$$C_{112}=L\left[0.3828Z^2+\frac{1}{9}(C_1+3B_1-3A_1)+\frac{1}{8}(C_2+3B_2-3A_2)\right] \tag{13}$$

$$C_{123}=L\left[6.1585Z^2+\frac{1}{9}(C_1+3B_1-3A_1)\right] \tag{14}$$

$$\frac{1}{L}C_{144}=6.1585Z^2+\frac{1}{9}(C_1+3B_1-3A_1)+\nabla\left[-3.3507Z^2-\frac{2}{9}C_1\right]+\nabla^2\left[-1.5637Z^2+\frac{2}{3}(A_1-B_1)+\frac{C_1}{9}\right]$$

$$\begin{aligned}\frac{1}{L}C_{166}&=-2.1392Z^2+\frac{1}{9}(C_1-6B_1-3A_1)+\frac{1}{8}(C_2-5B_2-3A_2)-(B_1-B_2)\\&+\nabla\left[-8.3768Z^2+\frac{2}{3}(A_1-A_2)-\frac{2}{9}C_1\right]+\nabla^2\left[2.3527Z^2+\frac{C_1}{9}\right]\end{aligned} \tag{15}$$

$$\begin{aligned}\frac{1}{L}C_{456}&=4.897Z^2+\frac{1}{9}(C_1-6B_1-3A_1)-B_2+\nabla\left[-5.0261Z^2-\frac{1}{9}C_1\right]\\&+\nabla^2\left[7.0580Z^2+\frac{1}{3}C_1\right]+\nabla^3\left[-4.8008Z^2+\frac{1}{3}(A_1-B_1)-\frac{1}{9}C_1\right]\end{aligned} \tag{16}$$

Various symbols appear in the earlier equations are associated with the crystal energy and have the following form:

$$A_1=A_{ij}=L'\left(\frac{d^2}{dr^2}U_{ij}^{SR}(r)\right)_{r=r_0} \tag{17}$$

$$A_2=A_{ii}=A_{jj}=L'\left(\frac{d^2}{dr^2}U_{ii}^{SR}(r)+\frac{d^2}{dr^2}U_{jj}^{SR}(r)\right)_{r=r_0} \tag{18}$$

$$B_1=B_{ij}=\frac{L'}{a}\left(\frac{d}{dr}U_{ij}^{SR}(r)\right)_{r=r_0} \tag{19}$$

$$B_2 = B_{ii} = B_{jj} = \frac{L'}{a}\left(\frac{d}{dr}U_{ii}^{SR}(r) + \frac{d}{dr}U_{jj}^{SR}(r)\right)_{r=r_0} \tag{20}$$

$$C_1 = C_{ij} = L'a\left(\frac{d^3}{dr^3}U_{ij}^{SR}(r)\right)_{r=r_0} \tag{21}$$

$$C_2 = C_{ii} = C_{ij} = L'a\left(\frac{d^3}{dr^3}U_{ii}^{SR}(r) + \frac{d^3}{dr^3}U_{jj}^{SR}(r)\right)_{r=r_0} \tag{22}$$

$$\nabla = \left[\frac{-7.5391Z^2 + (A_1 - B_1)}{-3.141Z^2 + (A_1 + 2B_1)}\right] \tag{23}$$

$$\Omega = -5.0440Z^2 + (A_1 + A_2) - 2(B_1 + B_2) \tag{24}$$

$$B_T = \frac{1}{3}(C_{11} + C_{12}) \quad \text{and} \quad \sigma = \frac{1}{2}(C_{11} - C_{12}) \tag{25}$$

In terms of short range energy

$$U_{ij}^{SR}(r) = b\beta_{ij}\exp\left(\frac{r_i + r_i - r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}^{\;6}} - \frac{d_{ij}}{r_{ij}^{\;8}} \tag{26}$$

With $L = \left(\frac{e^2}{4a^4}\right)$ and $L' = \left(\frac{4a^3}{e^2}\right)$.

Having discussed the effective interionic potential and its applications to various thermodynamical and elastic properties for chosen material.

6.3 Results and discussion

6.3.1 $Zn_{1-x}M_xSe$ (M: Cd, Fe and Mn) at high pressure

We have computed the structural phase transition pressures (P_t) following the technique of minimization of Gibbs free energies $G_{B3}(r)$ and $G_{B1}(r')$ for the equilibrium interionic spacing (r) and (r′) by using expressions (3) and (4).The values of r (r′) and corresponding cohesive energies U_{B3} (U_{B1}) for $Zn_{1-x}Mn_xSe$ have been obtained by us and depicted in Table 2 along with the phase transition pressures (P_t) and high pressure behaviour.

Table 3: Equilibrium separations and energies of $Zn_{1-x}M_xSe$ DMS. The values enclosed within parentheses correspond to their experimental values from ref. [20].

Solids	**Equilibrium lattice constant (Å)**		**Cohesive Energy (KJ/mol)**		**ΔU (KJ/mol) ($U_{B1}-U_{B3}$)**
	r (B_3)	r' (B_1)	U_{B3}	U_{B1}	
$Zn_{0.76}Mn_{0.24}Se$	2.5469 (2.4715)	2.845	-2292.	-2265.	27.00
$Zn_{0.84}Fe_{0.16}Se$	2.5195 (2.4416)	2.8107	-2306.	-2279.	27.00
$Zn_{0.9}Cd_{0.1}Se$	2.5223 (2.446)	2.8222	-2312.	-2287.	25.00

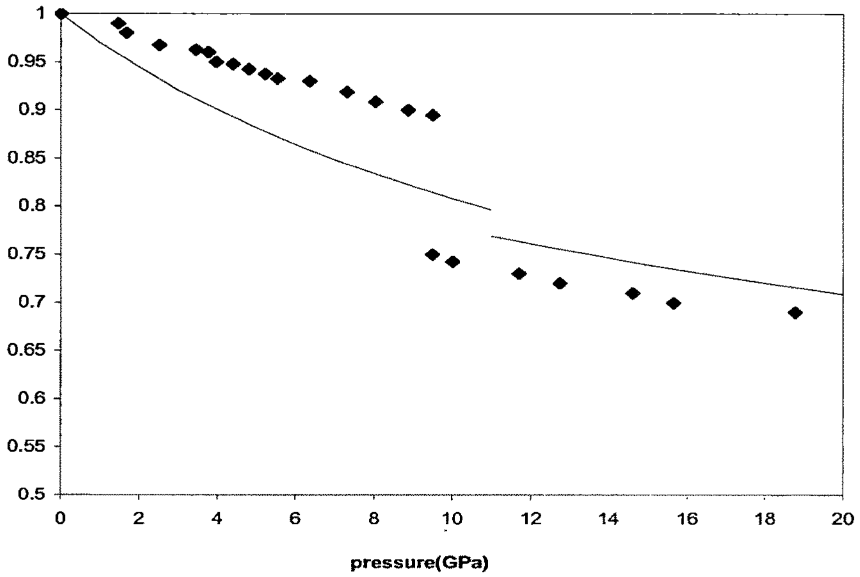

Figure.1: The equation of states of $Zn_{0.76}Mn_{0.24}Se$. The experimental data are from ref. [20].

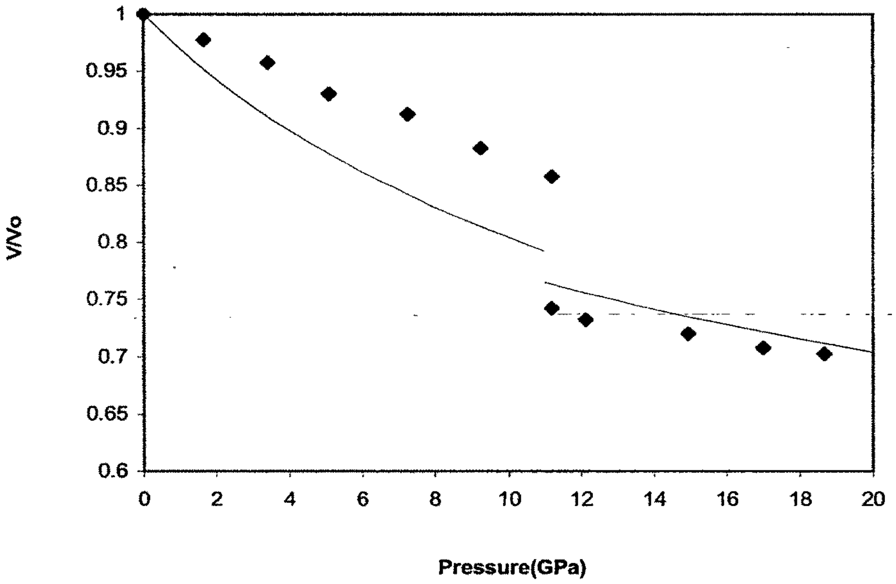

Figure 2: The equation of states of $Zn_{0.84}Fe_{0.16}Se$. The experimental data are from ref. [20].

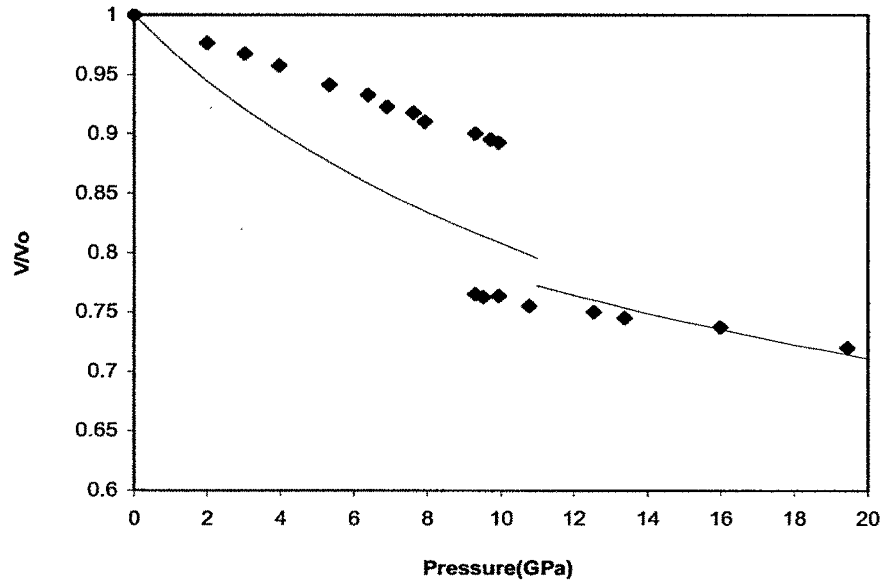

Figure3: The equation of states of $Zn_{0.9}Cd_{0.1}Se$. The experimental data are from ref. [10].

We have presented the calculated equation of states i.e. the relative volumes [V(p)/V (0)] against pressure for $Zn_{1-x}M_xSe$ and compared them with the available experimental data obtained by using EDXD [20] in Figures. 1-3. It is seen from figures and Table II that the values of phase transition pressure P_t obtained by us using the present approach are in good agreement with the experimental data [20]. The volume collapses [$\Delta V(P_t)/V(0)$] accompanied by phase transitions obtained from the compression curves for $Zn_{0.9}Cd_{0.1}Se$, $Zn_{0.84}Fe_{0.16}Se$ and $Zn_{0.76}Mn_{0.24}Se$ and presented in Table III and compared with experimental data. The present values of percentage volume collapses are not in very good agreement with the experimental data [20], which might be due to the exclusion of covalency effect in the interatomic potential.

Table 4: Phase transition pressure P_t (GPa), Relative Volume Change ($\Delta V(P_t)/V(0)$) (%), Shear to Bulk modulus ratios at phase transition. The values in parenthesis are from the experimental data [20].

Solids	P_t (GPa)	($\Delta V(P_t)/V(0)$) (%)	C_{44}/B
$Zn_{0.76}Mn_{0.24}Se$	10.4 (9.6±0.5)	2.7 (16.3)	0.50
$Zn_{0.84}Fe_{0.16}Se$	10.7 (11.94 ±0.5)	2.7 (13.5)	0.52
$Zn_{0.9}Cd_{0.1}Se$	10.3 (9.5 ± 0.3)	2.3 (16.1)	0.52

The values of the second order elastic constants and their combinations have been computed by using the expressions reported in ref. [36]. The values of second order elastic constants (not reported here) have been used to compute anisotropy factor (A) at ambient conditions by using the expression $A = (C_{11}-C_{12})/2C_{44}$. The computed anisotropy factors for $Zn_{1-x}Mn_xSe$, $Zn_{1-x}Fe_xSe$, $Zn_{1-x}Cd_xSe$ are 0.6319, 0.6254, 0.6333 respectively which shows that the materials will show anisotropy in its elastic properties, which is however not very high. Another remarkable feature, which can be seen from the calculated value of anisotropy, factors for these compounds are that the elastic isotropy in ZnSe is not sensitive to the effect of different substitutions, particularly considered here.

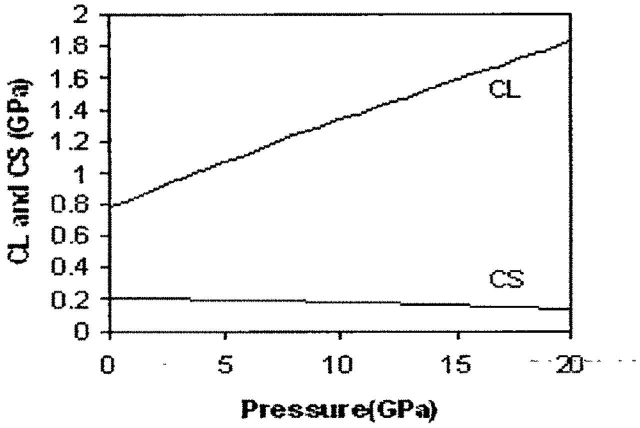

Figure 4: The variation of the combinations of elastic constants with pressure for $Zn_{0.76}Mn_{0.24}Se$.

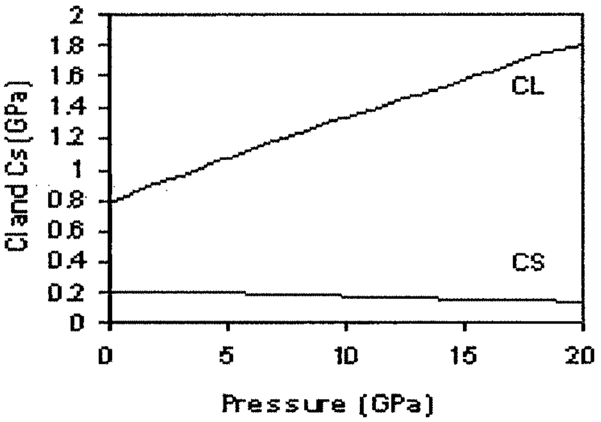

Figure 5: The variation of the combinations of elastic constants with pressure for $Zn_{0.84}Fe_{0.16}Se$.

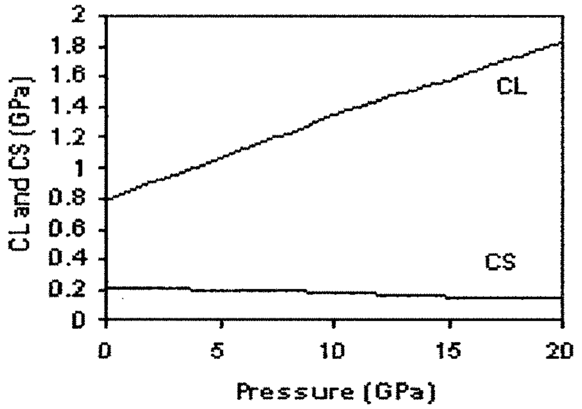

Figure 6: The variation of the combinations of elastic constants with pressure for $Zn_{0.9}Cd_{0.1}Se$.

We have plotted in Figs. 4-6, the variation of the combination of second order elastic constants $C_L = (C_{11}+C_{12}+2C_{44})/2$ and $C_S = (C_{11}-C_{12})/2$. These figures show that the pressure dependence of elastic constants for these compounds follow the similar trend as expected in the case of zinc blende structure semiconductor compounds and are in accordance with the first order character of the transition [31, 37]. In order to test the Born stability criterion [38], we have calculated the dimensionless ratios of shear to bulk modulus (C_{44}/B) at phase transition pressures (P_t) for $Zn_{1-x}Mn_xSe$ compounds and reported them in Table 4. The calculated values of C_{44}/B are around 0.5 and they satisfy the Born stability criterion. It is seen from Table 3 that the present approach has correctly predicted the relative stability of the crystal structure for $Zn_{1-x}Mn_xSe$ as the values of ΔU ($U_{B1}-U_{B3}$) are positive in all cases [38].

Table 5: Anharmonic properties of diluted magnetic semiconductors $Zn_{1-x}Mn_xSe$. Third order elastic constants C_{ijk} are in GPa. Values in parenthesis are from ref. [20].

Properties	**$Zn_{0.76}Mn_{0.24}Se$**	**$Zn_{0.84}Fe_{0.16}Se$**	**$Zn_{0.9}Cd_{0.1}Se$**
C_{111}	-2.04	-1.86	-1.93
C_{112}	-2.71	-2.59	-2.64
C_{123}	-1.32	-1.10	-1.16
C_{144}	-0.31	-0.42	0.40
C_{166}	-1.49	-1.47	-1.49
C_{456}	-0.90	0.96	0.96
$Kp = dB/dP$	2.40 (4.37± 0.16)	2.01 (4.12 ± 0.19)	2.01 (4.32 ± 0.18)
$Sp = dS/dP$	-0.54	-0.52	-0.53
$Cp = C_{44}/dP$	0.48	0.40	0.42

To the best of our knowledge, we have calculated for the first time the anharmonic properties, which include the evaluation of third order elastic constants (C_{ijk}) and pressure derivatives of (C_{ij}) by using the expressions from ref. [36] for $Zn_{1-x}Mn_xSe$ and reported them in Table 5. These values could not be compared with any data except the derivatives of bulk modulus as they are not available so far. Thus at present, these data are only of academic interest and discussion will be defended until a report of any experimental or theoretical data. However, the large discrepancy in dB/dP might by partly due to the exclusion of bond bending and bond stretching of covalent bonds which play an important role in the description of anharmonic properties of zinc blende compounds [12].

6.3.2 Mechanical, elastic and anharmonic properties of $Zn_{1-x}Cr_xTe$

We also report for the first time the results on the investigation of mechanical, elastic and anharmonic properties of ferromagnetic $Zn_{1-x}Cr_xTe$ for concentration $0 \leq x \leq 1$ including SOEC, TOEC, pressure derivatives, Debye temperature, specific heat, anisotropy, shear modulus etc. by using a theoretical model discussed above.

Table 6: Second order elastic constants, Anisotropy factor and Shear modulus for zinc blende $Zn_{1-x}Cr_xTe$ ($0 \leq x \leq 1$).

Concentration	**Elastic Constants (10^{11}dyne/Cm^2)**			**Anisotropy Factor A**	**Shear Modulus S (10^{11}dyne/cm^2)**
	C_{11}	C_{12}	C_{44}		
ZnTe	7.321[a] 7.110[b] 7.110[c]	4.259[a] 4.070[b] 4.070[c]	2.404[a] 3.130[b] 3.130[c]	0.6367	0.1530
$Zn_{0.8}Cr_{0.2}Te$	7.131	4.145	2.343	0.6371	0.1493
$Zn_{0.6}Cr_{0.4}Te$	6.975	4.015	2.337	0.6331	0.1480
$Zn_{0.4}Cr_{0.6}Te$	6.753	3.977	2.227	0.6231	0.1388
$Zn_{0.2}Cr_{0.8}Te$	6.538	3.781	2.172	0.6344	0.1378
CrTe	6.386	3.691	2.118[a] 3.64[d]	0.6359	0.1347

[a] From Our Present calculation. [b] From Ref. 35.
[c] From Ref. 42. [d] From Ref. 30-36.

The values of input parameter and obtained model parameters for $Zn_{1-x}Cr_xTe$ ($0 \leq x \leq 1$) are shown in Table 2. The second order elastic constants C_{11}, C_{12} and C_{44} have been obtained by using expressions from ref. [35] and are shown in the Table 5. The results obtained on the elastic constants from the present approach are in good agreement with the available experimental data [39-40]. It can be seen from the Table 5 that elastic constants decrease with the increase of Cr concentration. The obtained results on elastic constants are used to calculate the value of anisotropy factor A and shear modulus S which is about 0.62 and 0.15 respectively.

$$A = (C_{11}-C_{12})/2\,C_{44} \quad \text{and} \qquad S = (C_{11}-C_{12})/2 \qquad (27)$$

These values show that these compounds are having anisotropy in their elastic properties. We have also calculated the Debye temperature for $Zn_{1-x}Cr_xTe$ for different concentration of Cr using the following expression [41]:

$$\theta_D = C_B\,(a\,G_B/M)^{1/2} \quad \text{where} \quad G_B = [C_{44}(C_{11}-C_{12})(C_{11}+C_{12}+2C_{44})]^{1/3} \qquad (28)$$

Where a is a lattice constant and M is a atomic weight , $C_B = 3.89 \text{ X } 10^{11} \text{ X } S^{-1/6}\ h/K_B$ with h as Planck's constant and K_B as Boltzmann constant. S is a number of atoms per unit cell. The value of Debye temperature presented in Table 7 could not be compared for all value of x (Cr concentration). However, the value of Debye temperature obtained for ZnTe by using the present simple approach is in general good agreement with the available data. It can be seen from the table that the value of Debye temperature obtained for the different value of x are very close to the Debye temperature value of ZnTe and no much variation is observed. However, the Table 7 depicts the decrease in the Debye temperature of these compounds with the increase of Cr concentration, which implies that the lattice is getting, soften with the increase of Cr concentration. This can be in fact supported by the fact that the lattice parameters of Cr doped ZnTe increases with the increase of Cr. As far as the success of the approach in predicting the Debye temperature is concerned, we cannot make any comment at this stage but will emphasize for the specific heat measurement or the determination of the elastic constants for these compounds. We have also calculated the anharmonic properties such as TOEC and Pressure derivatives of SOEC i.e. dB/dP, dS/dP and dC_{44}/dP for $Zn_{1-x}Cr_xTe$ using the expressions presented in ref [36]. These results could not be compared with the experimental data due to unavailability. The calculated third order elastic constants and the pressure derivatives of elastic constants are listed in Table 7.

Table7: Debye temperature, Third order elastic constants (x 10^{11} dyne/cm^2) and Pressure derivatives of $Zn_{1-x}Cr_xTe$ ($0 \leq x \leq 1$).

Parameter	ZnTe	$Zn_{0.8}Cr_{0.2}Te$	$Zn_{0.6}Cr_{0.4}Te$	$Zn_{0.4}Cr_{0.6}Te$	$Zn_{0.2}Cr_{0.8}Te$	CrTe
θ_D (K)	185.27[a] 180±6[b] 225.3[c]	184.77	185.718	183.22	183.058	182.78
C_{111}	-20.26	-19.70	-18.59	-18.52	-17.69	-17.33
C_{112}	-25.18	-24.50	-23.45	-23.19	-22.82	-21.7
C_{123}	-14.90	-14.46	-13.32	-13.52	-12.82	-12.56
C_{144}	0.704	0.710	1.101	0.753	0.865	0.828
C_{166}	-13.04	-12.69	-12.32	-12.00	-11.58	-11.32
C_{456}	6.607	6.449	6.515	6.147	6.020	5.873
dB/dP	2.5048[a] 5.04[c]	2.5004	2.4088	2.4818	2.4472	2.4541
dS/dP	-0.589	-0.5892	-0.5797	-0.5872	-0.5837	-0.584
dC_{44}/dP	0.6757[a] 0.45[c]	0.6734	0.6247	0.6635	0.6452	0.6488

[a] From Our Present Calculation [b] From Ref. 35. [c] From Ref. 42.

6.4 Conclusion

In this chapter, we have systematically investigated the structural phase transition, high pressure behavior and anharmonic properties of ZnSe compound doped with Cd, Fe and Mn ions by using a theoretical approach which considers the effect of charge transfer due to the overlap of neighboring ions in the crystal energy. The results obtained for $Zn_{0.9}Cd_{0.1}Se$, $Zn_{0.84}Fe_{0.16}Se$ and $Zn_{0.76}Mn_{0.24}Se$ are in general good agreement with the available experimental data. The deviation in agreements might be due to the exclusion of the effect of covalency in these compound semiconductors. We have seen that the stability criterion has been satisfied for these compounds. The calculations show that the zinc blende structure is more stable for all these three compounds.

We also report the mechanical elastic and anharmonic properties of $Zn_{1-x}Cr_xTe$ ($0 \leq x \leq 1$). Obtained results agree fairly well with the experimental data wherever they are available. Debye temperature decreases with increase in concentration of Cr at room temperature. Obtained value of anisotropy predicts that material will be anisotropic in elastic behavior. The decrease of Debye temperature with the Cr concentration suggests that these compounds get soften with the increase of Cr concentration. Overall results are in good agreement with experimental values, which indicates success of our approach.

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