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Study of Phase Transitions in Chalcogenide Semiconductor Compounds (ChSCs) - $Cd_{1-x}Hg_xS$ at different Hg composition

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Abstract

The phenomena of structural phase transition in solids have been of great interest over decades. During this phenomenon crystals change their structures obeying certain thermo dynamical law. The application of pressure stabilizes the unusual valence states hinders diffusion and dislocations, affects the kinetics of chemical reactions and modifies mechanical properties of engineering materials. The II-VI compound semiconductors are relatively not new but very interesting class of materials in bulk as well as nano dimensions due to its wide applications in electronic industry. The most extensively studied and thoroughly understood materials of this type are $A^{II} - B^{VI}$ alloys. The doping of Mn^{2+} in $II - VI$ semiconductors of Zinblende structure affects their electronic, optical and magnetic properties of [1-3]. In recent research, the CHSCS materials have received much attention due to their unique combination of semiconducting and magnetic properties. In the present work, the TBP Model described in previous chapter, has been used to predict the pressure induced phase transitions (from zincblende (ZB) to rock salt (RS) structure) in $II - VI$ *alloy* $Cd_{1-x}Hg_xS$ materials. General information on the phase transition and its thermodynamic classification along with an idea of experimental and theoretical methods of its investigation are given in this paper.

INTRODUCTION

There are only three model parameters, b, ρ, f(r), and f'(r) in the three body potential model discussed above. Out of these, f'(r), is the first order space derivative of the TBI parameters f(r), with 2a as the lattice constant. In order to determine the values of the model parameters for $A^{II}_{1-x}B_xZ$ alloys, the crystal structure along with the range of compositions and the mean cation-cation distance as a function of Hg mole fraction x, for binary compounds .The vdW coefficients which have been used for the present study are reported in Table 3. These values have been evaluated by using Slater Kirkwood variation (SKV) approach [63]. At various concentrations, the vdW coefficients have been obtained from Vegard's law applied to their corresponding values for the end point member of the alloys: $A^{II}Z^{IV}$, $(A = Cd, Zn, Hg$ and $Z = S, Se, Te)$.

The input data used for the determination of the model parameters, are reported in Table () in which the values of the second order elastic constants (SOECs) and the lattice constant (2a) are given for the telluride materials. The lattice parameters of all ChSCs ternary alloys obey Vegard's law, showing the linear dependence of lattice parameters on composition. One can express the lattice parameter for any composition in the form [1]

$$a = (1 - x)a_{II-VI} + x\, a_{II-VI} \qquad 1$$

Where a_{II-VI} and a_{II-VI} are lattice parameters of the binary constituents (e.g., of CdTe and of hypothetical zincblende HgTe).

The input data for some other concentrations (x) for which the experimental data are not available have been obtained by model parameters have been determined by the use of SOECs in combination along with the equilibrium condition, and the expressions, which have been used are given below:

$$C_{11} = (e^2/4a^4)\,[\,0.2477\,Z(Z + 8f(r)) + (1/3)\,(A_1 + 2B_1) + (1/2)(A_2 + B_2) + 5.8243Zaf'(r)] \qquad 2$$

$$C_{12} = (e^2/4a^4)\,[-2.6458\,Z(Z + 8f(r)) + (1/3)\,(A_1 + 4B_1) + (1/4)(A_2 + 5B_2) + 5.8243Zaf'(r)] \qquad 3$$

$$C_{44} = (e^2/4a^4)\,[-0.1237\,Z(Z + 8f(r)) + (1/3)\,(A_1 + 2B_1) + (1/2)(A_2 + 3B_2) - (\nabla/3)\{-7.5391\,Z(Z + 8f(r))] + A_1 + B_1\}] \qquad 4$$

And the equilibrium condition:

$$B_2 + B_1 = -1.261\,Z(Z + 8f(r)) \qquad 5$$

Where,

$$\nabla = \frac{-7.5391\, Z\left(Z + 8f(r)\right) + A_1 - B_1}{-3.1446\, Z\left(Z + 8f(r)\right) + A_1 + 2B_1 + 21.7656\, Zaf'(r)} \quad 6$$

The value of the vdW coefficients (c_{ij}, d_{ij}) due to dipole-dipole (d-d) and dipole-quaderupole (d-q) interactions required for these calculations have been evaluated by using the Slater-Kirkwood Variation (SKV) approach [63]. Using then expressions and with their use if input parameters we have calculated the model parameters and cohasive energies for the solid solutions of Chalcogenide Semiconductor.

In order to study new the relative stability varies with pressure we calculate the cohesive energies ΦB_3 and ΦB_1 at different pressure and by using the minimization technique to obtained equilibrium inter ionic separation (r) associated with minimum energies and corresponding to a given pressure for B_3 and B_1 type phases respectively. The values of ΦB_3 and ΦB_1 for different volumes obtained by the present TBFP approach the tabulated in this Chapter along with the result obtained by others.

The pressure indicates the phase transition pressure at which the two phases stand in equilibrium. The Phase transition happened between two phases when the Gibbs free energy (G) of both the B_3 (B_1) type Phases is equal and the P_T is the pressure at which difference in free energies of two phase's ΔG approaches zero.

RESULTS AND DISCUSSION

For the computation of pressure dependence on various structural properties of mixed solid solutions TBI model has been applied and phase transition from original ZnS (B3) type phase to NaCl (B1) type has been observed. The computed values of various properties and parameters as results of TBI model applied on the solid solutions of ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, and HgTe have been reported in Tables from and graphically through Fig. 5.1 to 5.18

In the present thesis we have analysed various solid solutions of ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe. Viz.

$Zn_{1-x}Cd_x\ S, Zn_{1-x}Hg_x\ S, Cd_{1-x}\ Hg_x\ S,$
$Zn_{1-x}Cd_x\ Se, Zn_{1-x}Hg_xSe\ Cd_{1-x}\ Hg_x\ Se, Zn_{1-x}Cd_xTe, Zn_{1-x}Hg_x\ Te,$
$Cd_{1-x}Hg_x\ Te, ZnS_{1-x}Se_x\ CdS_{1-x}Se_x, HgS_{1-x}Se_x, ZnS_{1-x}Te_x, , HgS_{1-x}Te_x,$
$ZnSe_{1-x}Te_x\ HgSe_{1-x}Te_x$ etc.

Table 3. Calculated values of vdW coefficients for ChSCs

	C_{ii}	C_{ij}	C_{jj}	D_{ii}	D_{ij}	D_{jj}	C		D	
							B_1	B_3	B_1	B_3
ZnS	177.25	572.92	2352.42	480.49	4760.81	17297.69	6063.84	3458.79	36369.80	21668.65
ZnSe	177.25	659.30	3287.61	480.49	6280.41	27027.63	7478.34	4191.29	49600.75	29098.43
ZnTe	177.25	805.34	5348.97	480.49	9473.38	51720.38	10303.78	5612.82	79100.89	45247.70
CdS	1639.22	1937.52	2352.42	8678.87	16361.76	17297.69	16384.36	9957.94	110945.08	70023.34
CdSe	1639.22	2266.37	3287.61	8678.87	20889.79	27027.63	19398.07	11746.30	142664.97	89723.62
CdTe	1639.22	2831.73	5348.97	8678.87	30116.75	51720.38	24988.99	14993.71	209248.22	130483.74
HgS	5079.62	3448.47	2352.42	32505.53	30974.96	17297.69	29457.44	17848.36	210284.07	132642.64
HgSe	5079.62	4054.69	3287.61	32505.53	39140.17	27027.63	34300.44	20844.49	264357.01	167177.91
HgTe	5079.62	5103.48	5348.97	32505.53	55606.05	51720.38	43079.67	26196.93	375428.45	237463.38

For $Cd_{1-x}Hg_xS$ Alloys

Table 1a The input (*van der Waals coefficient(in units10^{-60} ergcm^6) and D(in units10^{-60} ergcm^6) interatomic separation ro(10^{-1}Nm)second order elastic constantC_{44}(Mbar), and Bulk modulus B_o*(Mbar), and model parameters (*range{b}, hardness{ρ} and TBI{f®}*) for $Cd_{1-x}Hg_xS$

$Cd_{1-x}Hg_xS$	C	D	r_o	C_{44}	B_o	b	ρ	f(r)
0	9957.94	70023.34	2.52	0.41	0.55	0.81	0.38	-0.77
0.25	11930.55	85678.17	2.52	0.38	0.58	0.79	0.38	-0.60
0.5	13903.15	101332.99	2.53	0.34	0.62	0.78	0.39	-0.43
0.75	15875.76	116987.82	2.53	0. 30	0.65	0.76	0.39	-0.26
1	17848.36	132642.64	2.53	0.26	0.69	0.74	0.39	-0.09

Table 1b The lattice parameter (r_0), Cohesive energies (Φ) of two competitive structures, difference in Free energy (ΔG), volume collapse [$-\Delta V(P_T)/V_0$]and Transition Pressure (P_T) for $Cd_{1-x}Hg_xS$

$Cd_{1-x}Hg_xS$	$r_0(10^{-1}Nm)$		φ(KJmole^{-1})		ΔG	$-\Delta V(P_T)/V_0$	P_T(GPa)
X	B_3	B_1	B_3	B_1			
0	2.52	2.72	-2440.00	-2392.20	47.80	0.13	3.30
0.25	2.53	2.67	-2154.75	-2104.40	50.40	0.11	4.18
0.5	2.53	2.63	-1869.50	-1816.60	53.00	0.09	5.05
0.75	2.53	2.58	-1584.25	-1528.80	55.60	0.06	5.93
1	2.53	2.54	-1299.00	-1241.00	58.20	0.04	6.80

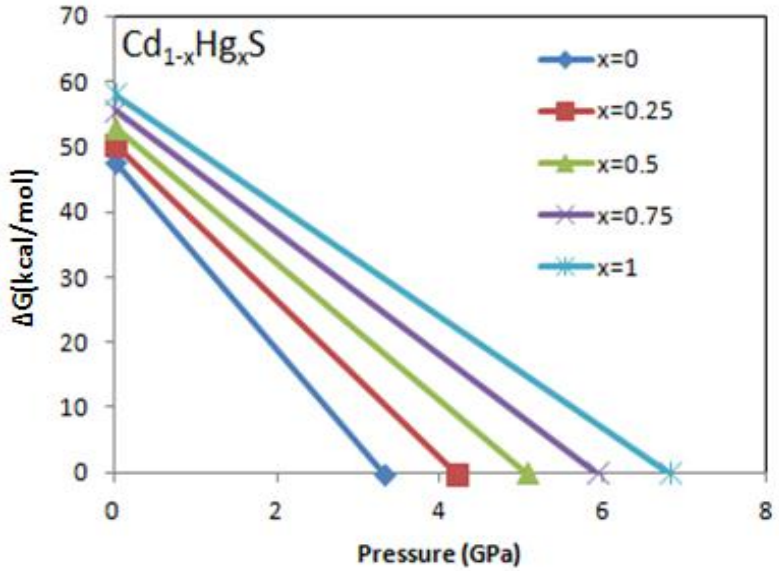

Figure 1. Phase Transitions in $Cd_{1-x}Hg_xS$ at different Hg composition (x)

The high pressure phase transition for $Cd_{1-x}Hg_xS$ have been analysed by using three body potential models applied at different Mercury concentrations. The model parameters ρ, b and f® have been computed through input parameters for host binary (CdS andHgS) and reported in Table 5.3(a). These model parameters have been used to compute the lattice energies (Φ) of two competitive structures at T=O K. Further the study has been made to observe the effect of pressure on interatomatic spacing (r_0), lattice energy (Φ), relative volume $[-\Delta V(P_T)/V_0]$ and morphology of the system. The relative volume factors $[-\Delta V(P_T)/V_0]$ were determined from the equilibrium inter nuclear separations in the crystals at P, evaluated by minimizing the Gibbs free energy. The computed values of variations in Gibbs free energy as a function of pressure for the various Hg compositions in the host CdS have been tabulated in Tables 1 (b). The lattice parameter (r_0), Cohesive energies (Φ) of two competitive structures, difference in Free energy (ΔG), volume collapse $[-\Delta V(P_T)/V_0]$ and Transition Pressure (P_T) for $Cd_{1-x}Hg_xS$ solid solution in B_3 and B_1 type structures have been reported in table 1 (b). The positive lattice energy difference ΔG as observed in the host binary as well as solid solutions are explains the Sangster criterion of structural stability. It is observed the transition from B3 to B1 type phase in the host binary CdS(HgS) and their solid solutions $Cd_{1-x}Hg_xS$ are given in Fig. 1 explains the understanding of phase transition, when change in Gibbs free energy ΔG reaches zero or negative. The plot of difference in Gibbs free energy as a function of pressure clearly confirms the phase transition phenomenon as and when it crosses the zero line. Another observation is the variation of transition pressure as a function of Hg composition in CdS binary, it is found that increase in Hg composition decreases the transition pressure for $Cd_{1-x}Hg_xS$ System in fig. 1. Looking at table 1(a-b) it can easily be observed that the lattice parameter and transition pressure follows the Vegard's law.

CONCLUSION

From the above discussion it is concluded for all the materials taken into consideration confirm the following:

* The correct description of r_0 confirms that the interactions considered in the presented computation and the process of the TBI model approach are capable of correctly predicting the minimum φ of ChSCs in the parental B_3 type phase as well as finally most stable hypothetical B_1 type phase and also the structural phase transitions.
* Well satisfied the Cauchy discrepancy criterion ($C_{12} \neq C_{44}$) supports the calculation accuracy of model parameters.
* The calculated r_0 for the B_3 type phase is slightly smaller than that for B_1 type phase, which seems to be correct and can be explained by the mechanism of the $B_3 \rightarrow B_1$ phase transition.
* The calculated φ for the B_3type phase is slightly smaller than that for the calculated φ for the B_1type phase, which seems to be correct and hence it satisfied the condition of structural $B_3 \rightarrow B_1$ phase transition.
* The calculation accuracy of bulk modulus (B_0), pressure derivative $(B_0)'$ supports the correct prediction of equilibrium cohesive energy (φ).
* The higher P_T well supports the higher hardness as well as stuffiness of $\mathbf{Cd_{1-x}Hg_xS}$.
* The TBFP approach is remarkable and in view of the constitutional simplicity and less parametric characteristic and hence a reasonable model for more realistic predictions of the relative structural stability, ground state properties (such as r_o, φ) and pressure induced structural phase transition of ChSCs based on the framework of semi classical theory.

A comprehensive assessment presented in this chapter show that the materials covered in this group are primarily ($CdTe, ZnTe, HgTe, ZnSe, HgSe, CdS, ZnS$ and HgS). With all this, TBI approach can be considered as the triumphant model potential to explain a variety structural property (such as r_0, φ) as well as structural phase transition of $\mathbf{Cd_{1-x}Hg_xS}$ in the present work, we could not be compare some prediction because of less availability of experimental/ theoretical information for this hypothetical compound, therefore, more experimental measurements and/or first-principles calculations are needed in order to obtain more accurate and reliable results. At present, our results might be of academic interest but we hope that the findings of this paper will certainly stimulate the work on the mixed $\mathbf{Cd_{1-x}Hg_xS}$ and may work as a guide to the experimental/theoretical scientists in future.

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