

Solid State Properties Of Rare Earth Monochalcogenides

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Abstract :

In this research paper semi-empirical simulation method has been evolved in order to evaluate solid state properties of a large range of rare earth monochalcogenides. Well established theory of J.C. Phillips, Van Vechten and Livine has been simulated in a very simple manner and unified expressions are evolved to evaluate a number of parameters such as homopolar gap, heteropolar or ionic gap, crystal ionicity, plasmon energy, electronic polarizability and bulk modulus etc. The result obtained are in a very fair agreement with reported data so far.

Keywords :

Ionicity, Polarizability, Plasmon energy, Energy Gap.

Introduction :

The extensive research devoted to the physics and chemistry of solids during the end of the last century has led to great advances the understanding of the properties of solids in general. Rare earth monochalcogenides (REX, RE = rare earth metals and X = S, Se, Te) have attracted the attention of physicists due to many practical uses, and have the rock salt crystal structures. During the last few years, frequent attempts have been made to understand the electronic properties of rare earth compounds. This is because of their interesting semi conducting properties and various practical applications in the field of non-linear optics, electro-optic components, glass-making, grinding alloys, composites lasers, phosphors lasers, and electronics [1–3].

The rare-earth monochalcogenides that crystallize in the NaCl-structure (fcc-lattice) have found considerable interest during the past years because they show promising optical, magnetic, and electrical properties [4,5]. An effective inter ionic interaction potential (EIIP) is developed to investigate the pressure-induced phase transition from NaCl-type (B1) to CsCl-type (B2) structure in Lanthanum monochalcogenides LaX (X = S, Se, and Te) compounds [6]. In addition, the validity of Born's mechanical stability criterion is checked by computing the second-order elastic constants. It is found that the high-pressure structures of LaX compound are stable [6]. From previous investigations it is found that the trivalent Lanthanum monochalcogenides LaX (X = S, Se, and Te) are superconductors near 1 K having transition temperatures in the range of 0.8–1.5.

Many researchers [7-11] have developed various theories and calculated the structural, electronic, optical and mechanical properties such as crystal ionicity, energy gaps, bulk modulus for rare earth monochalcogenides and pnictides. Phillips and Van Vechten's have calculated the homo polar and hetero polar contribution to the chemical bond in the binary solids. This theory is based on the simple one-electron model originally suggested by Penn and the model has used to separate the average energy gap into homo polar and hetero polar parts. The homo polar energy gap is taken to be a function of the nearest-neighbor

distance only. Levine has extended the Phillips and Van-Vechten (PVV) theory for ternary compounds considering also the effect of d core electrons.

Computational Method :

According to modified Phillips and Van-Vechten's [6-8] dielectric theory of solids, the average energy gaps (E_g) can be decomposed into a hetero polar or ionic parts E_c and homo polar or covalent part E_h , in the following form:

$$E_g = E_c + E_h \quad (1.1)$$

The covalent part E_h depends on the nearest neighbor separation d_{AB} as follows:

$$E_h = A d_{AB}^{-K_1} \quad (1.2)$$

where A and K_1 are the constants, i.e., remains unchanged in different crystals and have values $A = 40.468 \text{ eV}(\text{Å}^0)^{-2.5}$ and the exponent $K_1 = 2.50$. The corresponding values obtained by Phillips and Van Vechten [9,10,11,12] were $A = 39.74$ and $K_1 = 2.48$. The ionic contribution is inversely proportional to the nearest neighboring distance between atoms as:

$$E_c = b e^2 (Z_A - Z_B) d_0^{-1} \exp(-K_s d_0) \quad (1.3)$$

where Z_A and Z_B are the valence states of atoms A and B , respectively, d_0 is the one-half of the inter-atomic distance (d_{AB}) between atoms A and B and b is an adjustable parameter. The values of b depends on the co-ordination number around the cations, i.e. $b = 0.089 N_c^2$, where N_c – the co-ordination number. For rock salt type structure $N_c = 6$ and $b = 3.204$. The Thomas–Fermi Screening parameter (TFSP) K_s is defined as-

$$K_s = 2a_0^{0.5} (3N_c / \pi V)^{1/8} \quad (1.4)$$

where a_0 is the Bohr radius and V - the unit cell-volume. The crystal ionicity of chemical bond is expressed in terms of fractional ionic character (f_i) as follows:

$$f_i = E_c / E_g \quad (1.5)$$

The physical meaning of Eq. (1.3) is that E_c is given by the difference between the Screened Coulomb Potentials of atoms A and B having core charges Z_A and Z_B . These potentials are to be evaluated at the covalent radii d_0 . Only a small part of the electrons are in the bond, the rest screen the ion cores, reducing their charge by the Thomas–Fermi screening factor $\exp(-K_s d_0)$, which affects the chemical trend in a compound. This screening factor, as well as the bond length, is related to the effective number of free electrons in the valence band. The ionic charge also depends directly on the effective number of free electrons in the valence band. Thus, there must be some correlation between the physical process, which involves the ionic contribution E_c to the average energy gap (E_g), ionicity (f_i), electronic polarizability (α_e) and bulk modulus (B) and the plasmon energy (χ_p) of a compound.

Recently, Verma et al. [12,14,15,16,17] has shown that the crystal ionicity, electronic polarizability and bulk modulus of zinc blende and rock salt structured binary semiconductors may be determine in terms of the product of ionic charge and nearest neighbor distance d (in Å) by the following form-

$$B = A (Z_1 Z_2)^V d^3 \quad (1.6)$$

$$\alpha_e = A^* (Z_1 Z_2)^{V^*} d^3 \quad (1.7)$$

where A, V, A^* and V^* are the constants, which depends upon the crystal structure.

In this research work a simple expressions for the optical, electronic, static and dynamical properties such as bulk modulus (B), cohesive energy (E_{coh}), refractive index (n), polarizability (a) and optical susceptibility (ν) of zinc blende and wurtzite structured binary solids in term of plasmon energy (ω_P , in eV) by the following expression as-

$$B = M(\omega_P)^{2.333} \quad (1.8)$$

$$Z = N(\omega_P)^{1.333} \quad (1.9)$$

where M and N are constants, which depends upon the various type of crystal structure. Using this idea to get better agreement with the experimental data and theoretical values for the ionic gap (E_c), average energy gap (E_g), crystal ionicity (f_i), electronic polarizability (α_e) and bulk modulus (B) of rare earth monochalcogenides in rock-salt

structured may be written in terms of plasmon energy ω_P (in eV) as-

$$E_c = D(\omega_P)^{1.33} \quad (1.10)$$

$$E_g = S(\omega_P)^{1.41} \quad (1.11)$$

$$f_i = D^*(\omega_P)^{0.16} \quad (1.12)$$

$$\alpha_e = S^*(\omega_P)^{2.82} \quad (1.13)$$

$$B = D^t(\omega_P)^2 \quad (1.14)$$

where D, S, D^* , S^* and D^t are constants for rare earth monochalcogenides, which depends upon the various type (di- and trivalent) crystal structure of compounds and are presented in Table 1.1.

Table 1.1

In this table, the values of constants, are presented which are used in relations (1.10–1.14).

Constants	D	S	D^*	S^*	D^t
Divalent ($R^{+2}X$)	0.1578	0.1418	1.238	15330	0.282
Trivalent ($R^{+3}X$)	0.1188	0.1157	1.054	21382	–

Table 1.2

The present values of energy gaps, crystal ionicity, polarizability and bulk modulus of rare earth (R⁺²X) monochalcogenides.

Comp.	$\hbar \omega_p$ (in eV)	Energy gaps (in eV)				Crystal ionicity			Polarizability	Bulk modulus (in GPa)		
		Ionic gap				Avg. energy gap	f_i [this work]	f_i [PVV]	α_0 [Our] α_0 [Known*]	B [this work]	B _[Expt.] [33,34]	B _[Theo.] [5]
		E_c [this work]	E_c [PVV]	E_g [this work]	E_g [PVV]							
SmS	14.40	5.523	5.470	6.144	6.070	0.809	0.812	8.165	8.18	58.47	60	51
SmSe	13.60	5.118	5.209	5.667	5.724	0.815	0.828	9.598	9.32	52.16	52	45
SmTe	12.39	4.520	4.993	4.968	5.396	0.827	0.856	12.489	11.49	43.29	40	36
EuS	14.40	5.523	5.420	6.144	6.025	0.808	0.809	8.165	8.17	58.47	61 ± 5	51
EuSe	13.63	5.133	5.164	5.685	5.693	0.815	0.823	9.537	9.27	52.38	52 ± 5	46
EuTe	12.42	4.535	4.952	4.985	5.358	0.827	0.854	12.404	11.46	43.50	40 ± 5	37
TmS	16.64	6.145	6.353	6.879	7.181	0.797	0.783	5.427	6.80	68.63	—	—
TmSe	14.89	5.693	5.587	6.343	6.239	0.805	0.802	7.430	7.78	61.18	—	—
TmTe	13.54	4.868	5.415	5.375	5.912	0.820	0.839	9.718	10.09	48.39	46 ± 5	—
YbS	15.60	6.697	5.721	7.536	6.465	0.789	0.783	6.514	5.86	78.08	72 ± 5	63
YbSe	14.73	5.775	5.498	6.441	6.149	0.803	0.800	7.661	7.59	62.53	61 ± 5	54
YbTe	13.10	5.088	5.110	5.632	5.588	0.815	0.836	10.669	9.42	51.69	46 ± 5	41

* Calculated from the Clasiouss–Mossotti relation $\left[\frac{(\epsilon - 1)/(\epsilon + 2)}{\infty} \right] M / d - 2.53 \times 10^{24} \alpha_e$ taking n, M and d values.

Table 1.3

The present values of energy gaps, crystal ionicity and polarizability of rare earth ($R^{+3}X$) monochalcogenides.

Comp.	$\hbar \omega_p$ (in eV)	Energy gaps (in eV)				Crystal ionicity f_i [this work]	f_i [PVV]	Polarizability	
		Ionic gap		Avg. energy gap				a_e [this work]	a_e [Known*]
		E_c [this work]	E_c [PVV]	E_g [this work]	E_g [PVV]				
LaS	15.72	4.673	4.303	5.699	5.113	0.677	0.708	8.813	8.96
LaSe	14.94	4.367	4.125	5.280	4.840	0.683	0.726	10.26	10.05
LaTe	13.69	3.887	3.902	4.667	4.451	0.693	0.767	13.14	12.27
CeS	16.05	4.805	4.386	5.843	5.236	0.676	0.702	8.384	8.55
CeSe	15.21	4.472	4.200	5.416	4.936	0.681	0.724	9.758	9.66
CeTe	13.87	3.955	4.589	4.754	5.279	0.692	0.756	12.66	11.02
PrS	16.18	4.857	4.394	5.910	5.262	0.675	0.697	8.194	8.41
PrSe	15.35	4.527	4.204	5.486	4.970	0.680	0.716	9.510	9.46
PrTe	14.02	4.012	4.036	4.827	4.635	0.690	0.758	12.28	11.55
NdS	16.41	4.949	4.187	6.029	5.129	0.673	0.666	7.874	8.15
NdSe	15.54	4.602	4.247	5.582	5.037	0.679	0.711	9.186	9.20
NdTe	14.20	4.081	4.324	4.827	4.701	0.689	0.753	11.84	11.19
GdS	16.92	5.155	4.460	6.295	5.440	0.669	0.671	7.223	7.61
GdSe	16.10	4.825	4.282	5.869	5.150	0.675	0.691	8.309	8.56
GdTe	14.63	4.247	4.116	5.126	4.790	0.685	0.738	10.89	10.48
TbS	17.18	5.261	4.520	6.433	5.538	0.668	0.666	6.916	7.36
TbSe	16.24	4.881	4.324	5.941	5.217	0.674	0.687	8.109	8.32

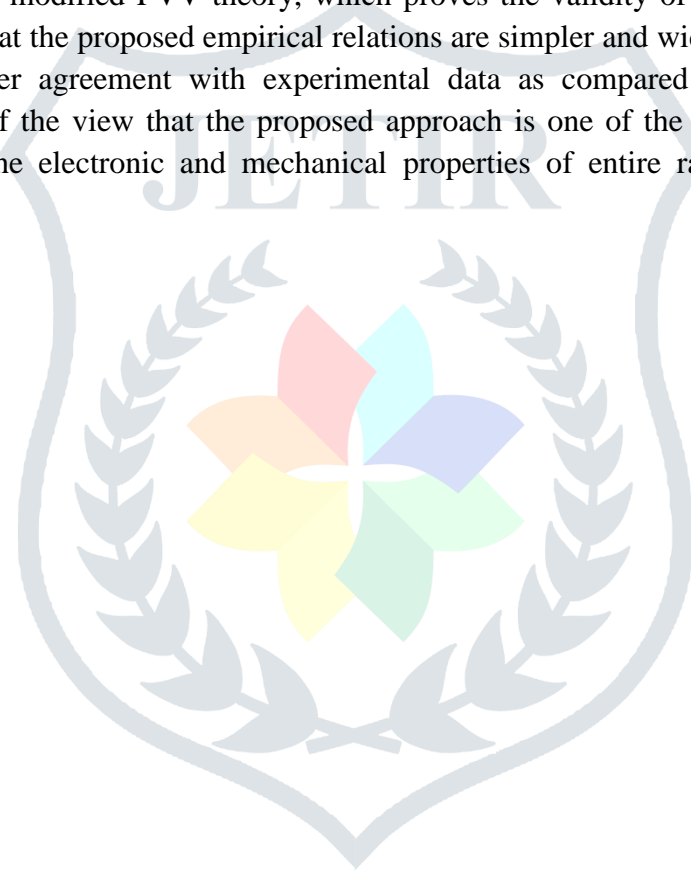
Comp.	ω_p (in eV)	Energy gaps (in eV)				Crystal ionicity f_i [this work]	f_i [PVV]	Polarizability	
		Ionic gap		Avg. energy gap				ϵ_e [this work]	ϵ_e [Known*]
		E_c [this work]	E_c [PVV]	E_g [this work]	E_g [PVV]				
TbTe		4.301	4.146	5.195	4.836	0.684	0.735	10.60	10.27
DyS	14.77	5.314	4.530	6.502	5.570	0.667	0.661	6.770	7.24
DySe	17.31	4.913	4.307	5.582	5.213	0.673	0.683	9.186	8.26
DyTe	16.32	4.344	4.150	5.250	4.854	0.683	0.731	10.38	10.13
HoS	14.88	5.359	4.543	6.560	5.602	0.666	0.658	6.651	7.13
HoSe	17.42	4.961	4.323	6.045	5.249	0.672	0.678	7.833	8.10
HoTe	16.44	4.379	4.160	5.295	4.877	0.683	0.729	10.20	9.99
ErS	14.97	5.433	4.558	6.565	5.646	0.665	0.652	6.641	6.98
ErSe	17.60	4.993	4.309	6.086	5.259	0.672	0.673	7.727	8.02
ErTe	16.52	4.422	4.163	5.350	4.893	0.682	0.724	10.00	9.84
LuS	15.02	5.553	4.464	6.812	5.681	0.663	0.618	6.168	6.73
LuSe	17.89	5.372	4.569	6.576	5.628	0.666	0.659	6.619	7.11
LuTe	17.45	4.693	4.354	5.699	5.166	0.677	0.710	8.813	8.89
	15.77								

* Calculated from the Clasiouss–Mossotti relation $\left[\frac{\epsilon(\infty)}{\epsilon(\infty)} \right] \left[\frac{\epsilon(\infty)}{\epsilon(\infty)} \right] M/d - 2.53 \times 10^{24} \alpha^e$, taking n, M and d values.

Electronic polarizability (α_e) and bulk moduli (B) for these materials has been calculated. The results are presented in Table 1.2 and 1.3. The calculated values are in excellent agreement with the experimental data and the values calculated by modified PVV theory. In the present model, the electronic and mechanical properties can be calculated by the plasmon energy as a key parameter alone.

Conclusion:

From the above results and discussion, we come to the conclusion that the valence electron plasmon energy of any compounds is a key parameter for calculating the electronic and mechanical properties. The ionic gaps, average energy gaps and bulk modulus of these materials directly related to the plasmon energy and crystal ionicity and polarizability is inversely related to it. The calculated values evaluated show a systemic trend and are consistent with the modified PVV theory, which proves the validity of the approach. It is also note worthy that the proposed empirical relations are simpler and widely applicable and values are in better agreement with experimental data as compared to the theoretical findings. We are of the view that the proposed approach is one of the best approaches in order to explain the electronic and mechanical properties of entire range of crystalline solids.



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