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Total energy, equation of states and bulk modulus of Si and Ge

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Abstract. A model potential describing electron-ion interaction is presented for intrinsic semiconductors Si and Ge. The present model potential is single parametric, continuous in r -space and weaker within core and Coulombic outside the core. The parameter of the potential is determined using the equilibrium condition at zero pressure. The total energy, equation of states and bulk modulus of Si and Ge are calculated using higher order perturbation theory based on pseudopotential formalism which includes covalent correction term. Numerical results of total energy and bulk modulus obtained for the Si and Ge are in good agreements with experimental data and found superior than other such theoretical findings. The predicted equation of states of Si and Ge are also excellent.

Keywords: pseudopotential method, semiconductors, binding energy, equation of states, bulk modulus

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1. Introduction

The second order perturbation theory based on the pseudopotential formalism has been applied to simple metals and their binary alloys, glasses and compounds with many successful examples [1-5]. However, the second order perturbation theory failed for covalent crystals because of covalent bonding character of these crystals. These difficulties were removed with the extension of the perturbation theory in terms of the pseudopotential by taking into account higher order terms corresponding to the covalent bonding effect [6-8]. The treatment of covalent crystals is difficult not because of complex structure of these crystals but mainly due to the determination of the model potential. Soma [9] used this higher order perturbation theory to calculate total energy and bulk modulus of IV semiconductors employing Ashcroft [10] empty core model potential. In addition to the usual potential parameter R_c , an adjustable additional parameter R_c' was used by Soma to ensure minimum energy condition in the first order perturbation energy [9]. He has also reported the results using the Heine-Abarenkov [11] model potential. In all such reported applications [9, 12], people have worked with historical model potentials like the Ashcroft and Heine-Abarenkov model potentials. Here, in the present paper, we extended the applications of our single parametric model potential [13] to investigate total energy, equation of states and bulk modulus of Si and Ge intrinsic semiconductors using the extended perturbation theory.

The analytical form of our model potential in r -space [13] is

$$W(r) = \begin{cases} -\frac{Ze^2}{R_c} \left[\frac{3r}{2R_c} - \frac{r^2}{2R_c^2} \right] & r < R_c \\ -\frac{Ze^2}{r} & r \geq R_c, \end{cases} \quad (1)$$

where Z is valency of the ion, e is the electronic charge and R_c the model potential parameter. The potential parameter R_c is determined by using zero pressure condition. The momentum-space representation of this model potential is given by

$$W_b(q) = -\frac{12\pi Ze^2}{\Omega q^3 R_c} \left[\frac{\sin(qR_c)}{2} - \frac{1}{qR_c} + \frac{\sin(qR_c)}{(qR_c)^2} \right]. \quad (2)$$

Where Ω is the atomic volume and q is the wave vector.

2. Computational method

For a covalent crystal with the diamond structure, based on the higher order perturbation theory, the total energy per electron of the crystal [6, 8] is given by

$$E = E_i + E_0 + E_1 + E_2 + E_{cov} \quad (3)$$

In equation (3), E_i is electrostatic energy of point ions immersed in the uniform gas of valence electrons, called the Madelung energy, which is given by

$$E_i = -\frac{\alpha Z^3}{r_s} \quad (4)$$

where r_s is the average interelectronic distance. The Ewald constant (α) for covalent crystals is 1.67085.

In equation (3), E_0 is the sum of the kinetic, exchange and correlation energies of the valence electron and is given by

$$E_0 = Z \left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} - (0.115 - 0.031 \ln(r_s)) \right] \quad (5)$$

E_1 is the first order perturbation energy of the valence electron due to the pseudopotential and is given by

$$E_1 = \lim_{q \rightarrow 0} \left[\frac{4\pi Z^2 e^2}{\Omega q^2} + ZW_b(q) \right] \quad (6)$$

For present pseudopotential, the value of the electron-ion interaction is

$$E_1 = \frac{9\pi Z^2 e^2 R_c^2}{10\Omega} \quad (7)$$

The second order term E_2 in equation (3) can be written as

$$E_2 = \sum_q |W_s(q)S(q)\chi(q)\varepsilon(q)| \quad (8)$$

where the summation \sum' excludes $q = 0$ and is carried out for 2006 reciprocal vectors. In above equation, structure factor of the diamond lattice is given by

$$S(q) = \sum_q \delta_{q,Q} \cos(q \cdot \tau) \quad (9)$$

where Q is the reciprocal vector and $\tau = (a/4, a/4, a/4)$ is a half of the vector in the body diagonal direction separating the two interpenetrating FCC lattices of lattice constant 'a'.

In equation (8), the pseudopotential screened by the electron gas is

$$W_S(q) = \frac{W_b(q)}{\varepsilon(q)} \quad (10)$$

The screening factor $\varepsilon(q)$ for a free electron gas is

$$\varepsilon(q) = 1 - \frac{8\pi e^2}{\Omega q^2} [1 - f(q)]\chi(q) \quad (11)$$

here $f(q)$ is the local-field correction and $\chi(q)$ is perturbation characteristics which is given by

$$\chi(q) = -\frac{3Z}{4k_F^2} \left[0.5 + \frac{1-X^2}{2X} \cdot \ln \left| \frac{1+X}{1-X} \right| \right] \quad (12)$$

where $X = \frac{q}{2k_F}$ and k_F is the Fermi wave vector.

The covalent bond correction (E_{cov}) corresponding to the third and fourth-order terms to the total energy is given by

$$E_{cov} = -n(E_F) \cdot \left[\left(\frac{a^2}{4\pi^2} \right)^2 W_S(111)^4 + \left(\frac{a^2}{2\pi^2} \right) W_S(220)W_S(111)^2 \right] \quad (13)$$

where the valence electron density of states per atom at the Fermi surface $n(E_F) = Z(2E_F/3)^{-1}$. In equation (13), $W_S(111)$ and $W_S(220)$ are the screened pseudopotential Fourier components at reciprocal points (111) and (220).

The equation of states and bulk modulus are obtained from

$$P = -\frac{dE}{d\Omega} \quad (14)$$

and

$$B = \Omega \frac{d^2E}{d\Omega^2} \quad (15)$$

In the present calculations, to determine R_c , the pressure less than 10^{-3} kbar is taken as equal to zero. For the incorporation of exchange and correlation effects to the dielectric function $\varepsilon(q)$, we adopted seven approximations, proposed by Hartree (H) [14], Hubbard and Sham (HB) [15,16], modified Hubbard Sham (HS) [15-17], Kleinman (K) [18], Kleinman and Langreth (KL) [18, 19], Vashistha and Singwi (VS) [20] and Taylor (T) [21].

3. Results and discussion

Tables 1 and 2 show the total energy per electron of semiconductors obtained by using equations (3-13) alongwith experimental and other such reported values [9, 12]. It is found from these tables that the effect of exchange and correlation is clearly distinguishable. The inclusion of exchange and correlation function suppresses the value of total energy of Si and Ge than those obtained by the static H dielectric function (without exchange and correlation). Thus, decrease in total energy due to inclusion of the exchange correlation to the dielectric function favors the cohesion of semiconductors. It is also predicted that the Taylor's $f(q)$ gives minimum energy for both Si and Ge.

Figures 1 and 2 show the pressure-volume relations for Si and Ge alongwith the experimental data [12]. The present finding of equation of states with various $f(q)$ is for Si and Ge at different volume are within the value obtained by inclusion of H and T local field correction to the dielectric function. Hence, to avoid the complication in the figures, equation of states obtained due to H and T are plotted. At 9% compression the effect of exchange and correlation function of T with respect to H is 25% for Si and 28% for Ge. Our equation of states for Si and

Table 1. Total energy E per electron of Si (in Rydberg units)

$f(q)$	Present [9]	Others [9]	[12]	[9]	Observed
H	-1.9413	-	-	-1.9758	-1.980
HB	-2.0458	-1.9758	-1.9882	-	
HS	-2.0440	-1.9734	-1.9859	-	
K	-2.0898	-1.9965	-2.0078	-	
KL	-2.0890	-1.9965	-2.0041	-	
VS	-2.1237	-2.0003	-2.0105	-	
T	-2.1463	-	-	-	

Table 2. Total energy E per electron of Ge (in Rydberg units)

$f(q)$	Present [9]	Others [9]	[12]	[9]	Observed
H	-1.8617	-	-	-1.960	-1.978
HB	-1.9608	-1.9418	-1.9663	-	
HS	-1.9605	-1.9404	-1.9647	-	
K	-2.0010	-1.9654	-1.9874	-	
KL	-2.0037	-1.9635	-1.9852	-	
VS	-2.0397	-1.9736	-1.9933	-	
T	-2.0597	-	-	-	

Ge are compared with the experimental data reported by Bridgman, Vaidya et al (by piston-cylinder method) and Senoo (by X-ray diffraction method)[12]. The excellent agreement for equation of states of Si and Ge is concluded in the present study.

The presently investigated bulk modulus (B) of semiconductors is tabulated in Tables 3 and 4 alongwith other such theoretical and observed data [6, 9]. The values in the parenthesis show the percentile deviation from the experimental data. From tables 3 and 4, it is noticed that the deviation of our result from observed values is 1.64% to 18.25% for Si and 2.14% to 33.79% for Ge. The results due to others [6, 9] include the deviation ranging from 14.72% to 31.59% for Si and 0.94% to 25.73% for Ge from the observed values. From Tables 1 to 4, we conclude that though the calculated values of total energy and bulk modulus of Si and Ge scatter in a bit wide range around the observed values, present findings are more improved results as com-

pared to previously reported other such theoretical values [6, 9, 12]. Thus, the present study confirms the fruitfulness of our model potential in predicting electronic properties of semiconductors. This also provides better set of theoretical results on total energy, equation of states and bulk modulus for intrinsic semiconductors Si and Ge for further comparison either with theoretical or experimental results.

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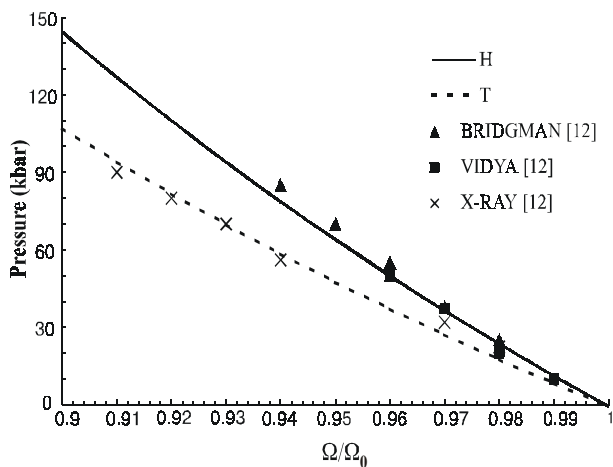


Fig. 1. The pressure-volume relations of Si

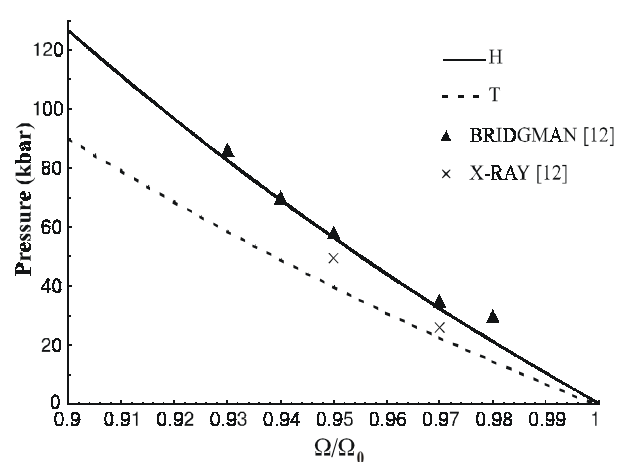


Fig. 2. The pressure-volume relations of Ge

Table 3. The bulk modulus of Si (in 10^{12} dyne/cm²)

$f(q)$	Present	Others			Observed [9]
		[6]	[9]	[9]	
H	1.1565 (18.25)	0.833 (14.83)	–	–	0.978
HB	1.0315 (5.47)	0.775 (20.76)	0.852 (12.88)	0.801 (18.1)	
HS	1.0041 (2.67)	0.729 (25.46)	0.834 (14.72)	0.780 (20.24)	
K	0.9940 (1.64)	–	0.810 (17.18)	0.754 (22.90)	
KL	0.9369 (4.20)	– (20.86)	0.774 (26.69)	0.717	
VS	0.9176 (6.17)	– (26.07)	0.723 (31.59)	0.669	
T	0.8625 (11.81)	–	–	–	

Table 4. The bulk modulus of Ge (in 10^{12} dyne/cm²)

$f(q)$	Present	Others			Observed [9]
		[6]	[9]	[9]	
H	1.0035 (33.79)	0.757 (0.94)	–	–	0.750
HB	0.8810 (17.17)	0.680 (9.33)	0.728 (2.93)	0.685 (8.67)	
HS	0.8554 (14.06)	0.654 (12.8)	0.717 (4.40)	0.662 (11.73)	
K	0.8455 (12.74)	–	0.704 (6.13)	0.646 (13.87)	
KL	0.7924 (5.65)	–	0.661 (11.87)	0.603 (19.60)	
VS	0.7661 (2.14)	–	0.615 (18.00)	0.557 (25.73)	
T	0.7218 (3.76)	–	–	–	

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