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AB-INITIO STUDY OF THE STABILITY OF $Si_{.5}Ge_{.5}$ SOLID SOLUTION

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AB-INITIO STUDY OF

THE STABILITY OF $Si_{.5}Ge_{.5}$ SOLID SOLUTION

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= To my parents =

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I. Introduction .

Recently, a significant progress in the calculation of the ground state properties of solids, within a unified theory based on non-local ab-initio pseudopotentials [1-3] and the local density approximation (LDA) [4-8], has been achieved. Very accurate results have been reported for many physical properties of pure materials [9-13] and some alloys [14] Our aim here is to discuss the application of this theory to study the stability and other properties of semiconducting alloys. $Si_{.5}Ge_{.5}$ solid solution has been taken as a prototype in this study. There are two motivations for this choice :

1. The study of the stability of materials with very useful properties such as Si-Ge solid solution is a fundamental and interesting subject by itself. Some experimental [15] and theoretical studies [16-18] exist in the literature. The theoretical work so far existing is not at the first-principle level.
2. The end materials (i.e., pure Si and pure Ge) are well known and extensively studied using this theory.

There are two kinds of disorder existing in such alloys :

1. Compositional disorder; in alloys (e.g. in the binary alloys A_xB_{1-x}) it is related to the disordered distribution of the A and B atoms in the lattice sites.
2. Structural disorder; while in (1) a perfect geometry of the lattice sites was assumed, in this case one considers distortions in bond angles and bond lengths.

Recent extended X-ray absorbtion fine structure (EXAFS) measurements have shown that three different bond lengths corresponding to the three possible pairs of atoms exist in these materials [19-20], which is a direct evidence of structural disorder in addition to the compositional disorder existing in such alloys.

In this work self-consistent calculations of the total energies as functions of the lattice constant have been carried out for Si, Ge and

$Si_{.5}Ge_{.5}$ solid solution within the virtual crystal approximation (VCA) and with the zinc-blend structure (ZBS). The results are least square fitted to Murnaghan's equation of state [9], to determine the minimum total energy, equilibrium lattice constant, bulk modulus and its pressure derivative at the equilibrium volume , for the four systems.

It should be emphasized that the structural disorder is copmletely neglected in this study (i.e., the perfect cubic geometry has been assumed for the alloys). While the compositional disorder is approximately taken into account by adopting the VCA, in which the diamond structure and one kind of pseudo-atoms having bare ionic potential equal to the average of that of Si and Ge are assumed.

The main results we have obtained are :

1. In agreement with experiment [15], we found that the mixture phase is preferable to the alloy phases. Where as , contrary to previous theoertical results[17-18], our calculations indicate that the ordered ZBS is more stable than the disordered phase within the VCA.
2. A good value for the deviation from Vegard's law is found within our simplified ZBS calculations.

This work is organized as follows, a very quick review about Si-Ge alloys, focusing only on the stability of these materials is given in Ch.(2) . Ch.(3) contains general background for calculating the ground state properties of solids. The details and the results of our work will be the subject of Ch.(4). And finally, a discussion of the results is given in Ch.(5).

II. Si_xGe_{1-x} Solid Solutions :

Si_xGe_{1-x} alloys received and are receiving an increasing interest, they have very useful properties which make them attractive for device applications [21], such as, low thermal conductivity at high temperatures, high mechanical strength, high melting point and resistance to atomospheric oxidation. Futhermore, recently hydrogenated amorphous Si_xGe_{1-x} alloys have been extensively studied and applied in efficient photovoltoic devices [20].

The lattice constant and the density for these materials have been studied experimentally by Dismukes et al. [22] and their values for the full range have been tabulated, the stability and the elastic properties by Bublik et al. [15], the thermal properties by Gauster [23], and the vibrational properties was the subject of a lot of experimental investigations [24-26], and theoretically using Bethe lattice by Agrawal [27]. A self - consistent band struture within the VCA, using the so called self - consistent plane waves model for $Si_{.5}Ge_{.5}$ alloys has been carried out, and compared with those of pure Si and pure Ge calculated by the same technique by Stukel [28]. Recently the variation of the band structure with composition using the k.p method within the VCA has been carried out [29].

Recent studies using the extended X-ray absorption fine structure(EXAFS) have shown that three different bond lengths corresponding to Ge-Ge, Si-Si and Si-Ge pairs of atoms exist in crytalline as well as amorphous Si_xGe_{1-x} alloys [19-20], which is a direct evedence of a structural disorder in addition to the compositional disorder existing in such materials. It has been pointed out by Zunger and Jaffe [30] that the structural disorder plays an important rule in the energy-gap bowing (i.e, the deviation of the gaps from linearity). We expect that it will be also important in studying the ground state properties of alloys.

Because of our interest here we will shed some light on what has been done so far to study the stability of these materials.

- The Stability of Si_xGe_{1-x} Solid Solutions :

The possibilty of `tailoring` optical and electronic properties makes the study of the semiconducting alloys of great interest, in particular the stability of these materials. A necessary condition for an alloy to be stable is that the difference in the free energy between the proposed alloy and the pure materials must be negative, which implies that at T = 0 the corresponding total energy difference must be negative . Only recently accurate first-principle calculation of the total energy has been achieved . In the past people used simple phenomenological theories based on spectroscopical data to study the stability of alloys . A predicion of the stability of Si_xGe_{1-x} alloys using a theory of this kind showed that at T = 0 these materials are not stable, and they become stable for all x when the temperature excedes 300° C [16] .

The energy of mixing has been determined expermentally from the intensity of diffuse X-ray scattering to be 5 ±.4 kcal/mole (or, .016 Ry/atom), the sign of the energy of mixing indecates that there is a tendecy to segregation in these materials [15] .

To our knowldge, theoretical study of the stability through total energy calculation has been done only by Bublik et al.[17], their work being based on perturbation theory. The Ashcroft pseudopotentials

$$V(r) = \begin{cases} 0 & \text{if} \quad r < r_c \\ \dfrac{-Ze^2}{r} & \text{if} \quad r > r_c \end{cases} , \qquad (2-1)$$

(where the parameter r_c has been determined from the form factors of Cohen and Bergstresser(CB)[31]) is used to represent the electron-ion interaction, and the Lindhard dielectric function within the random phase approximation (RPA) is used to account for the screening. Lately Soma[18] has extended this work by taking the exchange correction to the dielectric function into account, and using the Heine-Abarenkov pseudopotentials

$$V(r) = \begin{cases} -V_0 = \dfrac{-Ze^2}{r_c}u & \text{if} \quad r < r_c \\ \dfrac{-Ze^2}{r_c} & \text{if} \quad r > r_c \end{cases} \qquad (2\text{-}2)$$

where u and r_c are determined by fitting to the form factors of CB and the zero pressure condition

$$\left.\frac{dE}{d\Omega}\right|_{\Omega=\Omega_0} = 0 \ . \qquad (2\text{-}3)$$

Before discussing their results, we will digress to give breif description about the total energy calculation within the second order perturbation theory (SOPT), and its extension to account for the covalent nature of the bond in the case of semiconductors [32] .

In the SOPT the total energy of the system is given by

$$E_{tot} = E_{ion} + E_0 + E_1 + E_2 \ , \qquad (2\text{-}4)$$

where E_{ion} is the Ewald energy, E_0 is the sum of the kinetic, exchange and correlation energy of a free electron gas of density equal to the valence charge density, $\frac{E_1}{Z}$ is the average of the non-coulombic part of the bare electron-ion interaction, and E_2 represents the energy contribution due to the relaxation of the electrons in the non-uniform pitential, given by SOPT as

$$E_2 = \frac{\Omega_0}{16\pi} \sum_{G}{}' G^2 \left| W(G) \right|^2 \frac{1}{1-f(G)} \left(\frac{\varepsilon(G)-1}{\varepsilon(G)} \right), \qquad (2\text{-}5)$$

where $W(G) = S(G)V(G)$, here $S(G)$ and $V(G)$ are the structure and the form factors, respectively, $\varepsilon(G)$ is the dielectric function, $f(G)$ is the exchange correction and Ω_0 is the volume per atom .

It is well known that the SOPT is rather good for metals, but it gives unsatisfactory results in the case of semiconductors; this is due to the fact that the pseudopotentials are large in these materials compared with those of simple metals. Morita et al. [32] have extended this theory to covalent materials by adding to Eq. (2-2) a new term which takes into account the covalent nature of the bonds, their argument being based on the fact that the energy gap in the covalent materials are larger than $2|V(220)|$, the energy gap in the nearly free electron model. In semiconductors the energy gap is nearly constant over the Jones-zone faces except close to the edges and the corners; as an approximation they consider it to be a constant equal to the gap at $\underset{\sim}{K}=(110)$ (in $2\pi/a$ units) , which lies at the center of the Jones-zone faces and maps to the X point According to Heine and Jones [33] this gap can be given approximately by

$$E_k = 2\,V_{eff}(220) \quad , \quad \text{where} \qquad (\,2\text{-}6\,)$$

$$V_{eff}(220) = V(220) + \sum_{\underset{\sim}{G}}{}' \frac{\langle -\underset{\sim}{K}|V|\underset{\sim}{K}-\underset{\sim}{G}\rangle\langle \underset{\sim}{K}-\underset{\sim}{G}|V|\underset{\sim}{K}\rangle}{\underset{\sim}{K}^2 - (\,\underset{\sim}{K} - \underset{\sim}{G}\,)^2} + \dots$$

$$= V(220) + \frac{\{V(111)\}^2}{(110)^2 - (111)^2} \qquad (\,2\text{-}7\,)$$

The summation here is limited to the G-vectors which involve the strong form factor V(111) (i.e., only $(\bar{1}\bar{1}\bar{1})$ and $(\bar{1}\bar{1}1)$ G-vectors are taken into account). They argued that the correction term, which they called the covalent term can be given as

$$E_{cov} = -n(E_F)\left[|V_{eff}(220)|^2 - |V(220)|^2\right] \quad , \qquad (\,2\text{-}8\,)$$

where $n(E_F)$ is the density of electronic states at the Fermi surface, and this term is approximately equivalent to the inclusion of the third and fourth order terms.

Table (1) contains the results of Bublic et al. [15] , and for completeness the total energies of Si and Ge calculated using the same pseudopotentials are shown in table (2) . From these results one can draw several conclusions:

1. If we rely upon these results, then it is clear that the segregate phase is preferable by very small energy difference, and the disordered phase is more stable than the ordered zinc-blend structure (ZBS).

2. The covalent term E_{cov} is of order of the sum of the other electronic terms, since this term represents the third and the fourth order terms, it can serve as an indication that convergence has not been achieved .

3. It is difficult to accept that the large difference in the total energy of Si and Ge (see table (2)) is due only to the inclusion of the correction term only, and probably part of it is due the approach in which they have been calculated (i.e., the use of the perturbation theory) .

The work of Soma [18] has led to the same conclusions, and it is summarized in Fig. (1). It shoud be noticed that the broadening in the energy difference is due to the five approximations for the exchange correction used in that work.

Therefore, the current idea is that at T=0 the segregate phase is the stable phase, and the disordered phase (i.e., adopting the VCA) is more stable than the ordered ZBS for $Si_{.5}Ge_{.5}$ alloys .

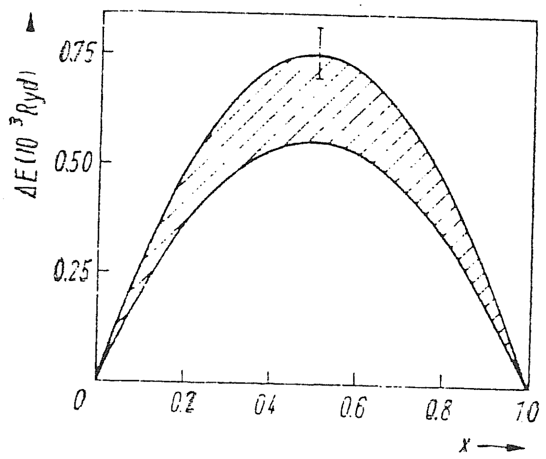

Figure 1. The total energy difference $\Delta E(x)$ between the mixture phase and the disordered solid solution within VCA. The mark at x = 0.5denotes the data $\Delta E(.5)$ for the ordered ZBS.

(After Ref. [18])

State	E_{ion}	E_o	E_1	E_2	E_{cov}	E_{tot}	E_{tot}
mixture .5Si+.5Ge	-8.2288	-.0504	1.6876	-1.0552	-.7124	-7.8296	
$Si_{.5}Ge_{.5}$(VCA)							
a_{Veg}(5.544)	-8.2268	-.0472	1.686	-1.0556	-.672	-7.8292	-.0004
a_{exp}(5.533)	-8.2436	-.0516	1.696	-1.0540	-.6584	-7.8228	-.0068
$Si_{.5}Ge_{.5}$(ZBS)							
a_{Veg}(5.544)	-8.2268	-.0472	1.686	-1.0548	-.672	-7.8288	-.0008
a_{exp}(5.533)	-8.2436	-.0516	1.696	-1.0536	-.6536	-7.8216	-.0076

Table 1. The total energy of $Si_{.5}Ge_{.5}$ solid solution, all energies are in Ry/atom. It should be noticed that the experimental lattice constant of the alloy is not the correct one (5.5373 A°) . (After Ref.(15))

E_{tot}	Si	Ge
RPA	-7.840	-7.736
Hubbard	-7.952	-7.856
Kleinman-Langreth	-7.984	-7.896
Experiment	-7.919	-7.912

Table 2. The total energy of pure Si and pure Ge calculated using three approximation for the exchange correction, along with the observed values. (After Ref. 32)

III. General Background For Calculating The Ground State Properties :

The calculation of the ground state properties of solids has advanced significantly in the recent years, it is possible now to carry out within a unified theory (based on a norm-conserving L-dependent pseudopotentials within the local density appoximation) accurate calculations of the static , dynamical and electronic ground state properties of solids [9-13] .

The fundamental quantity in this theory is the total energy. If one is able to calculate the total energy for a given ionic configuration, the calculation of the expermintally measurable quanties can be easily carried out. For example, by calculating the total energy of a given structure for few trial lattice constants, the minimum of the total energy corresponds to the equilibrium lattice constant. The bulk modulus and its derivative with respect to the pressure can be predicted by fitting the results to Murnaghan's equation of state [9]. By doing the same thing for other crystal structures, the stable structure and the solid-solid phase transition can be predicted . The derivative of the total energy with respect to structural parameteres, such as, the position of the ion and the strain tensor gives the forces involved in lattice dynamics (through Hellmann-Feyman theory [34]) and the stress tensor(through the stress theorem [35]), respectively. From the latter one can calculate the pressure (through the relation $P = -\frac{1}{3}\sum_{\alpha}\sigma_{\alpha\alpha}$, where $\overline{\sigma}$ is the stress tensor), which represent an alternative method for calculating the equilibrium lattice constant by imposing the condition that the pressure must vanish at equilibrium. From the stress and strain tensors one can calculate the elastic constants, from which the bulk and shear modulei can be calculated, and so forth.

The basic idea is to consider the distorted system as a completly independent system to be treated on equal footing as the undistorted one. The crucial physical concept which allows this is the adiabatic approximation, which is well verified in the case of semicondutors. Fixing the positions of the ions we left with the calculation of the electronic ground states, which is a many-body problem. The physical recipe to bypass this problem is to use the density functional theory, in particular the local density approximation[4-8] (LDA), which reduces the problem to solving a self-consistent one-particle Schrödinger type equation. It has been found that LDA gives accurate results for the ground state properties in comparison with the experimental results[9-13].

To carry out total energy calculation within LDA one can choose to work within the all-electron approach , or adopt the pseudopotential approximation. In the former approach all the electrons(valence and core) are treated on equal footing and the interaction between the electrons and the nuclei is purely coulombic, suitable numerical techniques known under the acronyms of LAPW and LTMO have been developed within this approach. In the pseudopotential appoach the core electrons are treated as frozen-electrons and valence electrons see an effective pseudopotential due to the nucleus and the core electrons. recently a norm-conserving L-dependent pseudopotentials have been constructed, which are able to reproduce the all-electron results in both the atomic and multiatomic systems[56]. The pseudopotential approach which is used in this work has two advantages over the other approach, first because of the relatively smooth nature of the pseudopotentials, it allows for the usage of the plane waves as basis, which are structure independent, easy to program and the convergace test can be done easily by increasing the cutoff. Secondly; because in the pseudopotential approach the large binding energy of the core electrons are not included in the total energy calculation, the total energy is two orders of magnitude smallar than the corresponding energy in the all-electron calculation. As a consequence it is easier to achieve high precision in the pseudopotential appoach needed for comparison purposes, which is essential in the calculation of the ground state properties.

This chapter will be organized as follows, in See.(1) we give a review about the density functional theory and LDA. Sec.(2) contains a brief discussion about the properties and the construction of the non-local pseudopotentials(NLPP). In Sec.(3) the solution of the Kohn and Sham (KS) equation is discussed . The total energy calculation is described in Sec.(4) . The summation over the filled state and the construction of a symmetrized charge density using the special points method are described in Sec.(6). Finally, in Sec(7) the choise of the cutoff is discussed.

3.1. The Density Functional Theory.

As we have pointed out the major difficulty after fixing the position of the ions is to find the electronic ground state for agiven ionic configuration. Which is a many-body problem , this problem is approximately solved in state-of-art semiconductor theory using the density functional theory of Hohenberg and Kohn[4-a]. They have demonstrated that if the ground state of the system is not degenerate, then the electronic charge density uniquely determines the external potential, and the electronic ground state energy as well; in other words the ground state energy is the variational minimum of the expression

$$E[\rho] = \int v_{ext}(r)\,\rho(r)\,dr + F[\rho] \qquad (3\text{-}1)$$

where $F[\rho]$ is a universal functional of the electronic density, and v_{ext} is the external potential. Kohn and Sham[4-b] reformulated the energy expression as

$$E[\rho] = \int V_{ext}(r)\,\rho(r)\,dr + \frac{1}{2}\int \frac{\rho(r)\,\rho(r')}{|r-r'|}\,dr\,dr' + T[\rho] \;\; E_{xc}[\rho] \qquad (3\text{-}2)$$

where the second term is the Hartree energy, the third term represents the kinetic energy of non-interacting electron system with electronic density $\rho(r)$, and the last term stands for the short-range e-e interaction energy, namely, the exchange and correlation interaction. This formalism is exact if $E_{xc}[\rho]$ is known, the most widely used appoximation to calculate this quantity is the local-density approximation[4-b]

$$E_{xc}[\rho] = \int \epsilon_{xc}[\rho(r)]\,\rho(r)\,dr \qquad (3\text{-}3)$$

where $\epsilon_{xc}[\rho]$ is the exchange and correlation energy per particle of a uniform electron-gas of density ρ . Finally, the electronic energy must satisfy the variational condition

$$\frac{\delta E[\rho]}{\delta \rho} = 0 \qquad (3\text{-}4)$$

at the correct charge density. It has been shown by Kohn and Sham[4-b] that this condition leads to a one-particle Schrödinger type equation known as Kohn-Sham equation (KS)

$$\left\{ -\frac{1}{2}\nabla^2 + V_{ext}(r) + V_H(r) + \mu_{xc}[\rho] \right\} \psi_i(r) = \epsilon_i \psi_i(r) ,$$

where

$$V_H(r) = \int \frac{\rho(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r}' , \text{ and}$$

$$\mu_{xc}[\rho(r)] = \frac{d(\rho(r)\,\epsilon_{xc}[\rho(r)])}{d\rho(r)} \qquad (3\text{-}5)$$

From Eq.(3-5) it is clear that the wavefunctions ψ_i depend on the charge density ρ ,which defined as

$$\rho(r) = \sum_i |\psi_i(r)|^2 \qquad (3\text{-}6)$$

Therefore, Eq.s (3-5) and (3-6) should be calculated self-consistently for ψ and ρ , when the charge density is known the electronic energy can be calculated using Eq.(3-2).

The total energy is calculated by adding the bare ion-ion interaction energy to the electronic energy, namely

$$E_{tot} = T[\rho] + \frac{1}{2}\int V_H(r)\,\rho(r)\,d\underline{r} + E_{xc}[\rho] + \int V_{ext}(r)\,\rho(\underline{r})\,d\underline{r} + E_{ii} \qquad (3\text{-}7)$$

It is worth to mention that this a general formalism valid for both all-electron and pseudopotential approaches. In the former V_{ext} is purely coulombic and the summation in Eq.(3-6) should be carried over the core and valence states. Whereas, in the latter approach the summation is over the valence states only, and V_{ext} in this case is the superposition of an effective interactions seen by the electron due to the presence of the ions (nuclei and core electrons). The core potential includes electrostatic as well as (non-classic) orthogonalization. The valence pseudo-wavefunctions are nodeless.

A new scheme for constructing ab-initio pseudopotentials from corresponding atomic calculations, which have optimum transferability among a variety of chemical enviroments has been suggested[1].

A useful set of pseudopotentials covring H to Pu have been constructed using the above scheme[3]. The properties and method of construction of such potentials will be the subject of the next section.

3.2. Ab-initio Pseudopotentials :

Hamann et al.[1] have suggested a scheme for extracting norm-conserving L-dependent pseudopotentials from ab-initio atomic calculation, which have optimum transferability to molecules and solids. Within this scheme the pseudopotentials are constructed as follows:

1. A screened L-dependent atomic pseudopotential V^{ℓ}_{sc} is constructed by inversion of the KS equation with the constraints: (a). The valence eigen-avlues obtained from all-electron and pseudopotential calculations agree for a chosen prototype atomic configuration. (b). The all-electron and the pseudo-nodeless-atomic wavefunctions agree beyond a chosen core radius r_c. Constraint (b) guarantees that the integral from 0 to r for all-electron and pseudo-atomic charge density agree for $r > r_c$ for the valence states (norm-conservation), which ensures through Gauss s theorem that the electro static potential produced outside r_c is identical for the two charge densities, and through the identity

$$-2\pi \left[(r\psi)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \psi \right]_R = 4\pi \int_0^R \psi^2 r^2 \, dr \qquad (3\text{-}8)$$

which ensures that the scattering properties(the phase shift which is related to the radial logarithmic derivative of ψ) have the same energy variation to the first order when trasfered to other systems.

2. To obtain the bare-ion pseudopotential the Hartree and the exchange and correlation potentials due the valence pseudo-charge density should be calculated and subtracted from V^{ℓ}_{sc} .

A full set of pseudopotentials using this scheme has been constructed and fitted in terms of simple analytical functions by Bachelet et al.[3]. The scalar relativistic pseudopotentials $\hat{V}^{ion}_{l}(r)$ defined as (following their notation)

$$\hat{V}^{ion}_{l}(r) = \frac{1}{2l+1} \left[l\, V^{ion}_{l-1/2}(r) + (l+1)\, V^{ion}_{l+1/2}(r) \right] \qquad (3\text{-}9)$$

have been given in the form

$$\hat{V}^{ion}_{l}(r) = \hat{V}_{core}(r) + \Delta \hat{V}^{ion}_{l}(r) \qquad (3\text{-}10)$$

where $V_{core}(r)$ is the local (L-independent) and long-range part of the potential, thought of as originating from Gaussian-type effective core charges and defined as

$$V_{core}(r) = -\frac{Z_v}{r}\left[\sum_{i=1}^{2} c_i \, \mathrm{erf}(\alpha_i^{1/2} r)\right] \tag{3-11}$$

The remaining short-range part is thought as non-local and given in the form

$$\Delta \hat{V}_l^{ion}(r) = \sum_{i=1}^{3} (A_i^{(l)} + A_{i+3}^{(l)} r^2 \; \exp(-\alpha_i^{(l)} r^2) \quad \text{for } l = 0,1,2 \tag{3-12}$$

and the higher angular momentum terms are thought as local and included in local part $V_{core}(r)$. In Fig's (1-2) we show the pseudopotentials of Si and Ge in rael space calculated using Eq.(3-11) and (3-12) with the constant A are calculated as desribed in Ref. (3).

3.3. The Solution of KS Equation.

After $V_{ext}(r)$ has been chosen, let us turn back to KS equation. The standered method for solving such equation is by expanding the wavefunction in terms of a basis set consisting of plane-waves(PW), or localized Gaussian orbitals, or a combination of both of them[37] The choice of the basis set depends on the potential (whither it has smooth or hard core) and the localization of the valence electrons of the system. The PW basis set works well in the case of smooth or relalively smooth pseudopotentials of a system with delocalized valence electrons (such as semiconductors), whereas, the second and the third basis sets are well suited for system with highly localized electrons (such as transition metals) and system with localized and delocalized electrons, respectively. In the case of all-electron and molecular calculations peaple usually use LAPW's or LMTO's .

Becouse of our interest here we will concentrate on the PW expansion of the wavefunction. Writing $\psi(r)$ as

$$\psi(r) = \frac{1}{\Omega^{1/2}} \sum_{G} C_G \, e^{i(G+q)\cdot r} \tag{3-13}$$

and multiplying Eq.(3-5) by $\psi^*(r)$ from the left-hand-side and integrating over all volume we obtain

$$\sum_{G'} \left[(q+G')^2 \delta_{GG'} + V_H(G'-G) + \mu_{xc}(G'-G) + \sum_{\alpha} S^{(\alpha)}(G'-G)\, V_{ext}^{(\alpha)}(q+G', q+G) \right] C_{G'} = \epsilon_i C_G$$

(3-14)

where S (G) is the structure factor of the atoms of type α , and $V^{(\alpha)}_{ext}(\underset{\sim}{q}+\underset{\sim}{G}', \underset{\sim}{q}+\underset{\sim}{G})$ is the matrix element of the pseudopotential of α atom between two plane waves, namely

$$V_{ext}(\underset{\sim}{q}+\underset{\sim}{G}', \underset{\sim}{q}+\underset{\sim}{G}) = \frac{1}{\Omega_{at}} \int \exp[-i(\underset{\sim}{q}+\underset{\sim}{G}')\cdot\underset{\sim}{r}]\, V_{ext}(\underset{\sim}{r})\, \exp[i(\underset{\sim}{q}+\underset{\sim}{G})\cdot\underset{\sim}{r}] \qquad (3\text{-}15)$$

where Ω_{at} is the volume per atom.

Now, the problem of solving KS equation is reduced to the solution of a set of algebric equations Eq.(3-15), the dimension of the secular equation to be solved is equal to the number of PW's included in the basis set. Experience has shown that more than 300 PW is needed if one wants a very good convergence for calculating the ground state properties of semiconductors [38] . When the $C_{\underset{\sim}{G}}$'s have been calculated starting from an emperical or uniform charge density, $\psi(r)$ and $\rho(r)$ can be easily determined, and used to calculate a new screening potentials(Hartree and X-C potentials) , this potential is then used to calculate new ψ (r) , and so on until good convergence is reached. The divergent term in the matrix elements of the pseudopotential when $G' = G$ which has the form $\frac{4\pi\bar{Z}}{\Omega_{at}G^2}$ (here $\bar{Z} = \sum_{\alpha} \frac{n_\alpha}{n} Z_\alpha$, where n_α is the number of atoms of type α , n is the total number of atoms in unit cell) must put equal to zero, this will lead to a constant shift in the eigenvalues, and should be compensated in the total energy calcultion as we will see in the next sectoin.

3.4. Total Energy Calculation .

As we have shown in Sec.(3.1), the total energy within the local density approximation is given as

$$E_{tot} = T[\rho] - \frac{1}{2}\int V_H[\rho]\rho(\underset{\sim}{r})\,d\underset{\sim}{r} + E_{xc}[\rho] + \int V_{ext}(\underset{\sim}{r})\rho(\underset{\sim}{r})\,d\underset{\sim}{r} + E_{ii} \qquad (3\text{-}16)$$

By multiplying Eq.(3-5) by ψ^* and integrating over the volume of the system and suming over all occupied state we obtain

$$\sum_i \varepsilon_i = T[\rho_{out}] + \int V_{ext}(\underset{\sim}{r})\rho_{out}(\underset{\sim}{r})\,d\underset{\sim}{r} + \int V_H[\rho_{in}]\rho_{out}(\underset{\sim}{r})\,d\underset{\sim}{r} + \int \mu_{xc}[\rho_{in}]\rho_{out}(\underset{\sim}{r})\,d\underset{\sim}{r} \qquad (3\text{-}17)$$

If a converged charge density has been achieved (i.e., $\rho_{in} = \rho_{out}$) we can make use of Eq.s (3-16) and (3-17) to obtain

$$E_{tot} = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2}\int V_H[\rho]\,\rho(\underset{\sim}{r})\,d\underset{\sim}{r} + \int[\epsilon_{xc}(\rho) - \mu_{xc}(\rho)]\,\rho(\underset{\sim}{r})\,d\underset{\sim}{r} + E_{ii} \qquad (3\text{-}18)$$

It should be emphasized again that this expression is meaningful only if the charge density is well converged. If not E_{tot} will be a function of the input and output charge densities . To make use of the variational property of E_{tot} with respect to ρ (i.e., to be correct to the second order with respect to the charge density) it must be a function of ρ_{out} only, we can make it so by replacing the first term in Eq.(3-18) by

$$\sum_i \varepsilon_i \rightarrow \sum_i \varepsilon_i - \int (V_H[\rho_{in}] - V_H[\rho_{out}])\,\rho_{out}(\underset{\sim}{r})\,d\underset{\sim}{r} - \int(\mu_{xc}[\rho_{in}] - \mu_{xc}[\rho_{out}])\,\rho(\underset{\sim}{r})\,d\underset{\sim}{r} \qquad (3\text{-}19)$$

In other words, we subtract terms which have explicit dependence on ρ_{in} and add corresponding terms calculated using ρ_{out} . After this has been done Eq.(3-18) takes the form

$$E_{tot} = \sum_i \varepsilon_i - \int (V_H[\rho_{in}] + \mu_{xc}[\rho_{in}])\,\rho_{out}(\underset{\sim}{r}) + \frac{1}{2}\int V_H[\rho_{out}]\,\rho_{out}(\underset{\sim}{r})\,d\underset{\sim}{r} + \int \epsilon_{xc}[\rho_{out}]\,\rho_{out}(\underset{\sim}{r})\,d\underset{\sim}{r} + E_{ii} \qquad (3\text{-}20)$$

The computational effort reduces significantly if the calculation of the total energy is carried out in momentum-space. It is easy to show by dierct Fourier-transform of Eq.(3-18) that the total energy per atom is given as

$$E_{tot}(\text{per atom}) = \frac{1}{N}\sum_i \varepsilon_i - \frac{1}{2}\Omega_{at}\sum_{\underset{\sim}{G}} V_H(\underset{\sim}{G})\,\rho(\underset{\sim}{G}) + \Omega_{at}\sum_{\underset{\sim}{G}}(\epsilon_{xc}(\underset{\sim}{G}) - \mu_{xc}(\underset{\sim}{G}))\,\rho(\underset{\sim}{G}) + \frac{1}{N}E_{ii} \qquad (3\text{-}21)$$

Because of the long-range nature of the coulomb interaction the $\underset{\sim}{G} = 0$ term in the first summation diverges as well as the ion-ion iteraction energy E_{ii} . Furthermore, if the first term is calculated with the divergent term in Eq.(3-14) put equal to zero, a third divergent term of the form $\Omega_{at}\left(\frac{-4\pi Z}{\Omega_{at}\underset{\sim}{G}^2}\rho(\underset{\sim}{G})\right)$ with $\underset{\sim}{G} = 0$ must be added to Eq.(3-21). This can be easily seen, since in this case the second term in the r.h.s. of Eq.(3-17) is not equal to the correspoding term term in Eq.(3-16). It has been shown through limiting procedure[39] that the sum of the divergent terms is finite and it is equal to the Ewald energy E_{ion} , which has been studied thoroughly in the literature[40] , and calculated as a function of a for many crystal structures[41] .

Therefore, Eq.(3-21) can be written as

$$E_{tot}(\text{per atom}) = \frac{1}{N}\sum_i \varepsilon_i - \frac{1}{2}\Omega_{at}\sum_{G\neq 0} V_H(G)\rho(G) + \Omega_{at}\sum_G (\epsilon_{xc}(G) - \mu_{xc}(G))\rho(G) + E_{ion} \quad (3\text{-}22)$$

Similarly, in momentum-space Eq.(3-20) takes the form

$$E_{tot}(\text{per atom}) = \frac{1}{N}\sum_i \varepsilon_i + \Omega_{at}\Big[\sum_{G\neq 0}[\tfrac{1}{2}V_H^{out}(G) - V_H^{in}(G)]\rho_{out}(G) + \sum_G [\epsilon_{xc}^{out}(G) - \mu_{xc}^{in}(G)]\rho_{out}(G)\Big] + E_{ion} \quad (3\text{-}23)$$

We have found that using this expression only about four iteration are needed to reach a convergence in the total energy better than 5 x 10^{-4} Ry per atom, which is half of the number of iterations needed if the non-variational expression is used .

3.5. Symmetrized Charge Density and Sum Over All Filled States :

To construct charge density and carry out the summation over all occupied states, one in principle needs to know their values at each point in the first Brillouin zone (BZ) or a fine mesh of points[42] , which is very time consuming. In the case of insulators and semiconductors, this can be avoided using the special points method, in which sets of a few special points (one[43], two or ten [44], or more[45]) are used. These sets of points are carefully selected to give a good approxiamtion over the BZ of the physical quantity of interest. The accuracy can be increased by increasing the number of points. It has been found that two or ten points is enough to give accurate results for semiconductors of diamond or ZB structure. In this scheme the symmetrized charge density is calculated through the formula

$$\rho(r) = \sum_{q_i} \omega_{q_i} \frac{1}{N_T}\sum_{\alpha\in T} \rho_{\alpha q_i}(r) \quad (3\text{-}24)$$

where W_{q_i} is a weighting factor associated to the special point q_i , α is a symmetry operation in the point group T of the crystal and N_T is the number of elements in T . It can be easily shown that the eigenvectors (i.e., the C_G's) of $\alpha^{-1}q$ (from which $\rho_{\alpha q_i}(r)$ is calculated) can be obtained from the corresponding eigenvectors of q through the relation

$$C_{n,\alpha^{-1}q}(\alpha^{-1}G) = C_{nq}(G \quad \exp[i(q+G)\cdot r(\alpha)] \quad (3\text{-}25)$$

where n is the band index and $\tau(\alpha)$ is the non-primitive translation associated with the symmetry operation α. Because of the time-reversal symmetry we have $\psi_{q}(r) = \psi_{-q}(r)$. This allows us to replace the point group O_h of the diamond crystal by the subgroup O of the ZBS. Since the point group O has no non-primitive translation associated with its symmetry operations Eq.(3-25) redduces to

$$C_{n,\alpha^{-1}q}(\alpha^{-1}G) = C_{n,q}(G) \tag{3-26}$$

The calculation of $\rho_{q}(r)$ from the corresponding eigenvectors can be done using the fast Fourier transform subroutines, as will be described in the next chapter.

Since the eigenvalues at each point of the star of q_i are equal, it follows that within the special-points method the first term in Eq.s(3-22) and (3-23) is replaced by

$$\frac{1}{N} \sum_{i} \varepsilon_i(q) \rightarrow \sum_{q_i} w_{q_i} \sum_{n,occ} \varepsilon_{n,q_i} \tag{3-27}$$

Therefore, in the final form Eq.s (3-22) and (3-23) can be written respectively as

$$E_{tot}(\text{per atom}) = \sum_{q_i} w_{q_i} \sum_{n,occ} \varepsilon_{n,q_i} + \Omega_{at} \left[\frac{1}{2} \sum_{G=0} V_H(G)\, \rho(G) + \sum_{G} \left(\epsilon_{xc}(G) - \mu_{xc}(G) \right) \rho(G) \right] + E_{ion} \tag{3-28}$$

$$E_{tot}(\text{per atom}) = \sum_{q_i} w_{q_i} \sum_{n,occ} \varepsilon_{n,q_i} + \Omega_{at} \left[\sum_{G\neq 0} \left[\frac{1}{2} V_H^{out}(G) - V_H^{in}(G) \right] \rho_{out}(G) \right.$$
$$\left. + \sum_{G} \left[\epsilon_{xc}^{out}(G) - \mu_{xc}^{in}(G) \right] \rho_{out}(G) \right] + E_{ion} \tag{3-29}$$

3.6. The Choice of The Cutoff .

The PW 's used in the expansion of the wavefunctions (see Eq.(3-13)) are usually chosen in such a way that each of them has kinetic energy less than a certain energy cutoff, namely $\frac{2\pi^2}{a^2}(q+G)^2 \leqslant E_{cut}$.

A thorough study of the convergence has been carried out by Holzschuh[38], it turns out that 300 - 400 plane waves are needed to get good convergence in the total energy for Si with the use of norm-conserving pseudopotentials. In the calculation of the ground state properties , such as, the equilibrium lattice constant, bulk modulus and so forth. The total energy as a function of a can be performed using a constant number of PW's or constant energy cutoff. The two curves in general do not coincide (i.e., they give different results) unless a good covergence in the Fourier-series expansion has been achieved. The choise of the constant energy cutoff is more physical since it corresponds to a constant resolution (i.e., a-independent) of the wavefunctions in real space. It has been domenstrated [46-47] that this choice gives in the incomplete convergence cases smaller errors in the equilibrium lattice constant, as shown in Fig. (2) .

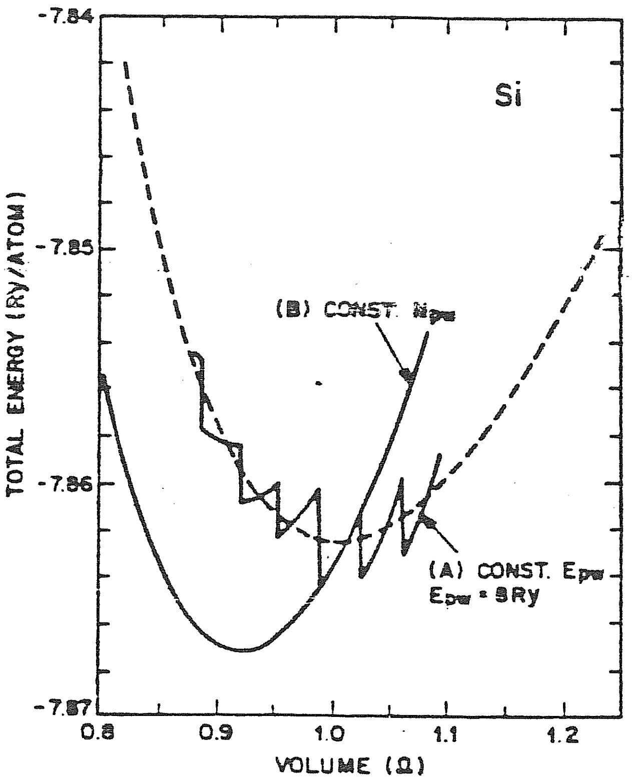

Figure 2. Total energy curevs of Si. Curve A use constant E_{cut} (= 8 Ry) and curve B use costant N_{PW} (= 104). The dashed curve is a least-square fit to Murnaghan s equation of state to curve A. (After Ref. 46).

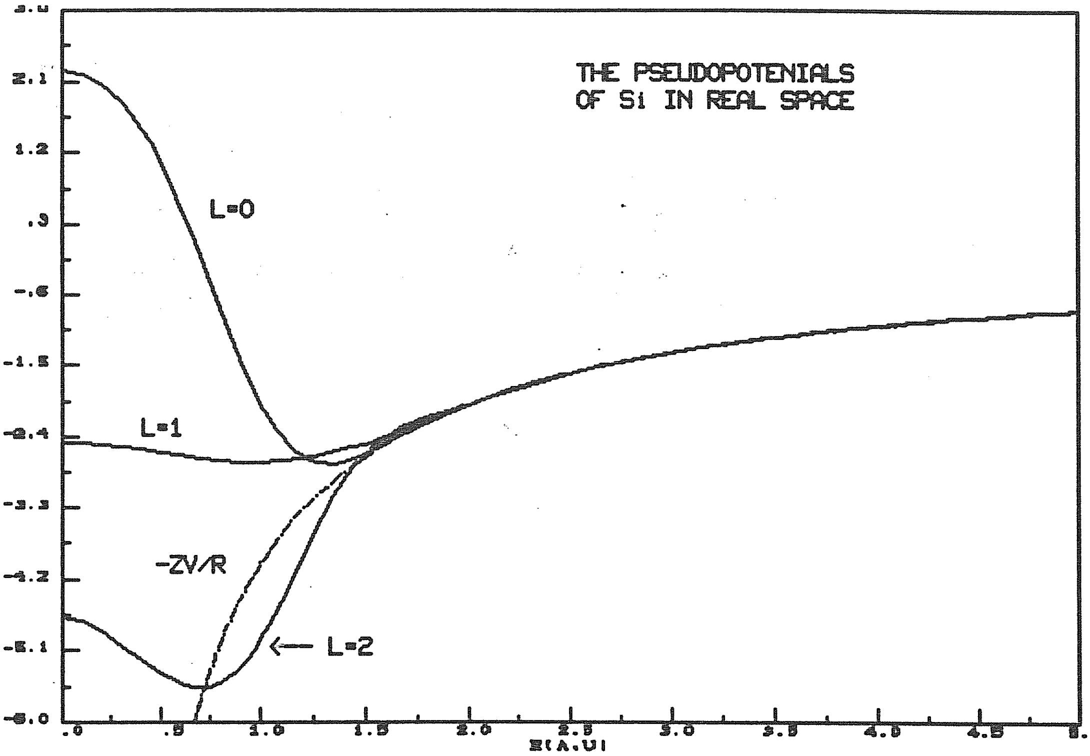

Figure 3. Bachelet et al.[3] pseudopotentials (in a. u.) of Si in real

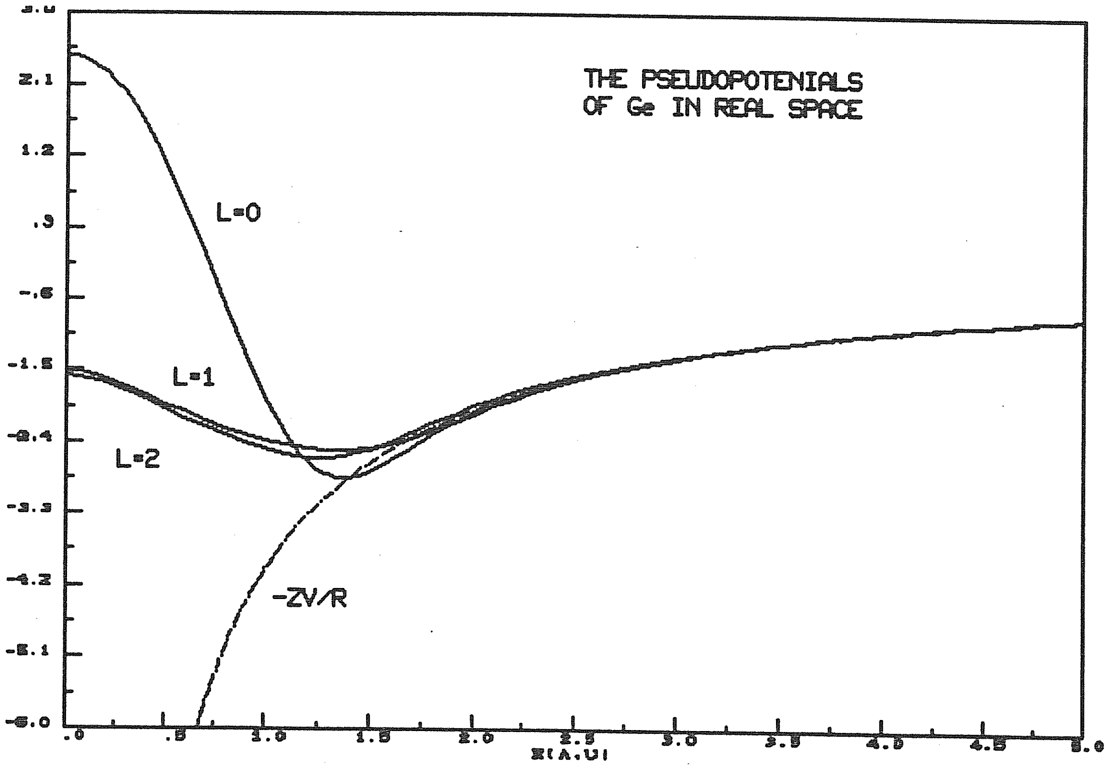

Figure 4. Bachelet et al.[3] pseudopotentials (in a. u.) of Ge in real space.

IV. Computational Details and Results .

Self-consistent calculations of the total energy as function of a have been carried out for Si, Ge and $Si_{.5}Ge_{.5}$ alloys. In this latter case, we have considered both the VCA and the ZBS . The norm-conserving pseudopotentials of Bachelet et al. [3] (NCPB) have been used in this work. The results are fitted to Muranghan's equation of state to determine the equilibrium lattice constants, bulk modulei and their pressure derivatives at the equilibrium volumes. In this chapter we will give the details and the results of our work.

Now, let us start with the KS equation. As we have shown in the last chapter, the solution of this equation can be reduced to the solution of a set of algebric equations Eq.(3-15). To build up these equations one needs the matrix-elements of V_{ext} between two plane waves and the FT of the Hartree and exchange and correlation potentials .

4.1. The Matrix-elements of NCPB Between Two PW's .

The scalar relativistic NCPB are decomposed into long-range part $V_{core}(r)$ given as in Eq.(3-11), and a short-range L-dependent part $\Delta\hat{V}_l(r)$ given as in Eq.(3-12). The matrix-element of $V_{core}(r)$ between two PW's as defined in Eq.(3-15) is just $V_{core}(\underset{\sim}{G}'-\underset{\sim}{G})$,where

$$V_{core}(\underset{\sim}{q}) = -\frac{Z_v}{\Omega_{at}}\left(\frac{4\pi}{\underset{\sim}{q}^2}\right)\left[\sum_{i=1}^{2} C_i^{core}\exp\left(\frac{-q^2}{4\alpha_i^{core}}\right)\right] , \qquad (4-1)$$

The matrix-element of the non-local part $\Delta\hat{V}_l(r)$ between two PW's can be written in the form

$$\frac{1}{\Omega_{at}}\int e^{-i(\underset{\sim}{q}+\underset{\sim}{G}')\cdot\underset{\sim}{r}}\,\Delta\hat{V}_l(r)\,e^{i(\underset{\sim}{q}+\underset{\sim}{G})\cdot\underset{\sim}{r}}\,d\underset{\sim}{r} = \sum_{i=1}^{3}\left(A_{li}\,I^{(1)}_{li} + A_{li+3}\,I^{(2)}_{li}\right),$$

where

$$I^{(1)}_{l,i} = \frac{1}{\Omega_{at}}(2l+1)\,P_l\left(\frac{K\cdot K'}{KK'}\right)\left(\frac{\pi}{\alpha_{li}}\right)^{3/2}\exp\left(-\frac{K^2+K'^2}{4\alpha_{li}}\right) i_l\left(\frac{KK'}{2\alpha_{li}}\right) \qquad (4-2)$$

here P_l and i_l are the Legendre polynomials and modified spherical Bessel functions of the Lth order, respectively. $\underset{\sim}{K}$ and $\underset{\sim}{K}'$ are $\underset{\sim}{G}+\underset{\sim}{q}$ and $\underset{\sim}{G}'+\underset{\sim}{q}$, respectively. Whence

$$I^{(2)}_{li} = -\frac{d}{d\alpha_i} I^{(1)}_{li} = \frac{1}{\Omega_{at}}(2l+1)\, P_l\left(\frac{\underset{\sim}{k}\cdot\underset{\sim}{k}'}{kk'}\right) \exp\left(-\frac{k^2+k'^2}{4\alpha_{li}}\right)\left(\frac{\pi}{\alpha_{li}}\right)^{3/2}\frac{1}{\alpha_{li}}\Big[$$

$$\left(0.5-l-\frac{k^2+k^2}{4\alpha_{li}}\right) i_l\left(\frac{kk'}{2\alpha_{li}}\right)+\frac{kk'}{2\alpha_{li}}\, i_{l-1}\left(\frac{kk'}{2\alpha_{li}}\right)\Big]. \qquad (4\text{-}3)$$

Therefore, the third term in the L.H.S. of Eq.(3-14) can be written as

$$\sum_{\alpha} S^{(\alpha)}(\underset{\sim}{G}'-\underset{\sim}{G})\,\gamma^{(\alpha)},$$

where

$$\gamma^{(\alpha)} = V^{(\alpha)}_{core}(\underset{\sim}{G}'-\underset{\sim}{G}) + \sum_{l=0}^{2}\sum_{i=1}^{3}\left(A_{li\alpha}\, I^{(1)}_{li\alpha} + A_{l\,i+3\,\alpha}\, I^{(2)}_{li\alpha}\right), \qquad (4\text{-}4)$$

where α here runs over the different types of atoms. Taking the origen to be on the center of the bond it takes the form:

a. In the case of pure Si and pure Ge

$$\cos((\underset{\sim}{G}-\underset{\sim}{G}).\underset{\sim}{r})\,\gamma \qquad (4\text{-}5)$$

(here the index α is supressed since there is only one kind of atoms)

b. In the case of the $Si_{.5}Ge_{.5}$ alloys within the VCA

$$\cos((\underset{\sim}{G}-\underset{\sim}{G}).\underset{\sim}{r})(\gamma^{Si}+\gamma^{Ge})/2 \qquad (4\text{-}6)$$

c. In the case of the $Si_{.5}Ge_{.5}$ alloys with ZBS

$$\cos((\underset{\sim}{G}-\underset{\sim}{G}).\underset{\sim}{r})(\gamma^{Si}+\gamma^{Ge})/2 + i\sin((\underset{\sim}{G}-\underset{\sim}{G}).\underset{\sim}{r})(\gamma^{Si}-\gamma^{Ge})/2 \qquad (4\text{-}7)$$

From Eq.'s (4-5),(4-6),(4-7) and (3-14) it is clear that the Hamiltonian matrices for pure materials and alloys within the VCA are real-symmetric matrices, whereas, for alloys with the ZBS they are complex-hermitian . We left to say that in the limit $\underset{\sim}{q}\to 0$, $V(\underset{\sim}{q})$ as given in Eq.(4-1) can be written as

$$\lim_{q\to 0} V_{core}(\underset{\sim}{q}) = \frac{-4\pi Z_v}{\Omega_{at}\, q^2} + \frac{\pi Z_v}{\Omega_{at}}\sum_{i=1}^{2}\frac{C_i^{core}}{\alpha_i^{core}}. \qquad (4\text{-}8)$$

In building up the Hamiltonian matrices only the first term (which diverges at $\underset{\sim}{G} = 0$) is put equal to zero, this leads to a constant shift in the eigenvalues, which is important for the calculation of the total energy. The second term is finite and is equal to the average of the non-coulombic part of the local part $V_{core}(r)$ of NCPB .

4.2. The Start Charge Density .

As start Hartree and exchange and correlation potentials , we used the potentials calculated from the valence charge densiyies obtained useing the form factors of CB in the case of Si and Ge, the form factors of Soma[18] (v(111) = -.1947 , v(220) = .0136 and v(311) = .0483) in the case of alloys within VCA. The self-consistent charge density obtained within the VCA is used to start the calculations in the case of $Si_{.5}Ge_{.5}$ alloys with ZBS at the same lattice constant .

Only one special point and about 100 PW's are used to build up the start potentials .

4.3. Calculation of $\rho(\underset{\sim}{r})$, $V_H(\underset{\sim}{G})$ and $\mu_{xc}(\underset{\sim}{G})$.

All the Brillouin-zone integration have been carried out using two special points of Chadi and Cohen in the irreducibale wedge ($\underset{\sim}{q}_1$ =(3/4, 1/4,1/4) and $\underset{\sim}{q}_2$ = (1/4,1/4,1/4) with weighting factors 3/4 and 1/4 , respectively) . As we have pointed out in the last chapter , the point group O of ZBS can be used instead of O_h the point group of diamond to calculate symmetrized charge density for the systems with diamond structure. This can be reduced further by considering only one symmetry operation among those which take the point $\underset{\sim}{q}_i$ to the same point $\underset{\sim}{q}_i'$, let T_i to be the reduced set of elements of $\underset{\sim}{q}_i$. Then, Eq.(3-24) can be written in the form

$$\rho(\underset{\sim}{r}) = \sum_{\underset{\sim}{q}_i} w_{q_i} \frac{N_O}{N_{T_i}} \cdot \frac{1}{N_{T_i}} \sum_{\alpha \in T_i} \rho_{\alpha \underset{\sim}{q}_i}(\underset{\sim}{r}) \qquad (4\text{-}9)$$

where N_O and N_{T_i} are the unmber of elements of O and T_i , respectively. It turns out that N_{T_i} is equal to twelve and four for the first and second points, respectively.

The cherge densities $\rho_{\underset{\sim}{q}_i}(\underset{\sim}{r})$ are the sums over occupied states of the square of the crystal-pseudo-wavefunctions $\phi_{n,\underset{\sim}{q}_i}(\underset{\sim}{r})$, which are nothing but the inverse FT of the eigenvectors $C_{n,\underset{\sim}{q}_i}(\underset{\sim}{G})$. Fast FT (FFT) subroutines have been used to calculate $\phi_{n,q_i}(\underset{\sim}{r})$, using a mesh of (20 x 20 x 20) points, the mesh is chosen in such a way that no ($\underset{\sim}{G}' - \underset{\sim}{G}$) used in building up the Hamiltonian matrices maps to a point outside the mesh. A test of convergence has been done using a mesh of (24 x 24 x 24) points, the same result of the total energy is reproduced for Ge with lattice constant 10.9 a.u. (the largist lattice constant we have used in this work), this ensures that a good convergence has been achieved .

When $\phi_{nq_i}(r)$ at aperiodic mesh of points are known, the charge density can be calculated easily

$$\rho_{q_i}(r) = \sum_{n,occ} |\phi_{nq_i}(r)|^2 \qquad (4\text{-}10)$$

To calculate the charge density $\rho_{\alpha q_i}(r)$ at other points of the star of q_i, the eigenvectors at these points are constructed from $C_{nq_i}(G)$ using Eq.(3-26), and then the above described procedure is followed to calculate $\rho_{\alpha q_i}(r)$. The symmetrized charge density $\rho(r)$ can be calculated using Eq.(4-9).

The exchange and correlation potential can be calculated at the points of the mesh from $\rho(r)$ through LDA, different approximations for the exchange and correlation potential are available , we used the electron-gas data of Ceperly and Alder [48] as parametrized by Perdew and Zunger[49].

Knowing $\rho(r)$ and $\mu_{xc}(r)$ at a mesh of points in real space, we used the FFT subroutines to calculate $\rho(G)$ with $\rho(r)$ as input and $\mu_{xc}(G)$ with the $\mu_{xc}(r)$ as input. The Hartree potential in momentum-space $V_H(G)$ has been calculated from $\rho(G)$ through the relation

$$V_H(G) = \frac{4\pi\,|\rho(G)|^2}{G^2} \qquad (4\text{-}11)$$

4.4. Cutoff.

In this work a constant energy cutoff E_{cut}= 17.5 Ry has been used, this leads to a different number of PW's for different special points and lattice constants. The average number of PW's used at each trial lattice constant are shown at the top of Fig.'s (5-8).

A considerably large E_{cut} has been used to reduce as much as possible the errors encountered in the truncation of the Fourier-space expansion of the wavefuctions. It should be mentioned that all the PW's having $|q+G|^2 \leqslant E_{cut}$ are included exactly in the calculations .

4.5. Convergence Accelaration .

To speed up the convergence in the self-consistent procedure, we have used a simple mixing scheme, in which the input screening potential of the (n+1)th iteration is taken to be a linear combination of the input and output potentials of the nth iteration .

$$V_{in}^{(n+1)} = \alpha\, V_{in}^{(\kappa)} + (1-\alpha)\, V_{out}^{(n)} \qquad (4\text{-}12)$$

we used $\alpha = 1/2$.

4.6. Calculation of The Total Energy .

The total energy calculation has been carried out using Eq.(3-29). As usual the Ewald energy is expressed in the form $E_{ion} = -\alpha \frac{Z^2}{a}$, where $\alpha = 5.386816$ [38] for crystals with diamond structure, it takes the same value for $Si_{.5}Ge_{.5}$ alloys within the VCA and with the ZBS(this is becouse the bare pseudo-charges are equal to 4 in all cases). The calculation of $\epsilon_{xc}(G)$ has been done in the same manner as $\mu_{xc}(G)$ descirbed in Sec.(4.3) . It should be emphasized that symmetrization is not needed for the first term of Eq.s (3-28) and (3-29). Finally, we have to say that 1400 $\underset{\sim}{G}$-vectors are used to carry out the summation in the total energy expression.

Starting with suitable charge density as we have shown in Sec.(4.2) , about four iterations are needed to reach convergence better than 5×10^{-4} Ry per atom in the total energy.

The results are least-square fitted to Murnaghan's equation of state

$$E_{tot}(V) = \frac{B_0 V}{B_0'} \left(\frac{(V_0/V)^{B_0'}}{B_0'-1} + 1 \right) + const \qquad (4\text{-}13)$$

where B and B_0 are the bulk modulus and its pressure derivative at the equilibrium volume V_0 . The results of the fitting compared to the available experimental data are given in table (3) for the four systems. The total energy as function of a are shown in Fig. (5-8) .

To domenstrate the advantage of using the variational expression to calculate the total energy, we have calculated a well converged charge density for Si at the observed value of the lattice constant in two steps :

1. Starting with charge density calculated from the form factors of CB, the self-consistent procedure has been carried out until a convergence better than 5×10^{-4} Ry/atom in the total energy has been achieved. In this step the variational expression is used in to calculate the total energy .

2. Starting with the charge density we end with in step (1) , we continue with the self-consistent porcedure,using the non-variational expression this time to calculate the total energy until the same convergence has been achieved again .

It turns out that four iterations are needed to reach the convergence in the first step, and it takes other four iterations to converge to the same value of the total energy in the second step.

The FT of the start and converged charge densities along with with the one we end with after step (1) and the convergence are shown in table (4). From this table it is clear that a well converged charge density is not necessary condition to reach a good convergence in the total energy if the variational expression has been used.

		Lattice constant (A)	Bulk modulus (Mbar)	B'_0	E_{tot}(min) (Ry/atom)	$\| E - E \|_{max}$ (Ry/atom)
Si	Cal.	5.378	.98	4.6	-7.93432	8.82×10^{-5}
	Exp.	5.431	.99	4.2	-7.91900	----
Ge	Cal.	5.572	.77	4.9	-7.98171	4.27×10^{-5}
	Exp.	5.657	.77	4.6	-7.91200	----
$Si_{.5}GE_{.5}$	Cal. (VCA)	5.490	.87	4.6	-7.94910	2.77×10^{-5}
	Cal. (ZBS)	5.470	.87	2.4	-7.95737	7.56×10^{-5}
	Exp.	5.537	---	----	----	----
	Ave. (Exp.)	5.544	---	----	----	----

Table 3; Comparison of calculated ground state properties of Si, Ge and $Si_{.5}Ge_{.5}$ Within VCA and having ZBS with the available experimental data. the last column contains the maximum deviation between the calculated E_{tot} and that obtained from Muranghan's equation of state. The average of the experimental lattice constant is also shown.

$\underset{\sim}{G}$	$\rho(\underset{\sim}{G})$ (start)	$\rho(\underset{\sim}{G})$ (step 1)	$\rho(\underset{\sim}{G})$ (con.)	Convergence
0 0 0	8.0000000	8.0000000	8.0000000	0.0000000
1 1 1	-1.6029405	-1.7895143	-1.7872926	0.0000695
0 2 2	0.2642800	0.0613958	0.0621557	0.0000211
1 1 3	0.4318875	0.3488845	0.3487526	0.0000143
2 2 2	0.4673422	0.3613012	0.3606564	0.0000251
0 0 4	0.2364660	0.3828159	0.3829734	0.0000026
1 3 3	0.0255647	-0.0393979	-0.0396298	0.0000075
2 2 4	-0.0050610	-0.1587489	-0.1588347	0.0000064
3 3 3	0.0015649	-0.1354073	-0.1354664	0.0000162
-1 1 5	0.0003446	0.0932653	0.0932979	0.0000063
0 4 4	0.0195782	-0.0628894	-0.0625854	0.0000012
1 3 5	0.0097214	-0.0430396	-0.0429414	0.0000004
2 4 4	0.0075870	-0.0274455	-0.0274227	0.0000032
0 2 6	0.0053591	-0.0274033	-0.0272750	0.0000001
3 3 5	0.0023321	-0.0049490	-0.0050001	0.0000003
2 2 6	0.0023008	-0.0067835	-0.0067531	0.0000014
4 4 4	0.0003885	-0.0021777	-0.0022677	0.0000007
1 5 5	-0.0000771	-0.0074320	-0.0074992	0.0000001
-1 1 7	0.0006502	0.0005246	0.0006669	0.0000015
-2 4 6	-0.0001030	0.0089028	0.0089789	0.0000003

Table 4. Fourier components $\rho(\underset{\sim}{G})$(in electrons/cell) of the start, after step 1 (see text) and the converged valence charge densities of Si. The absolut difference between $\rho(\underset{\sim}{G})$ after the last interation and one before is also shown.

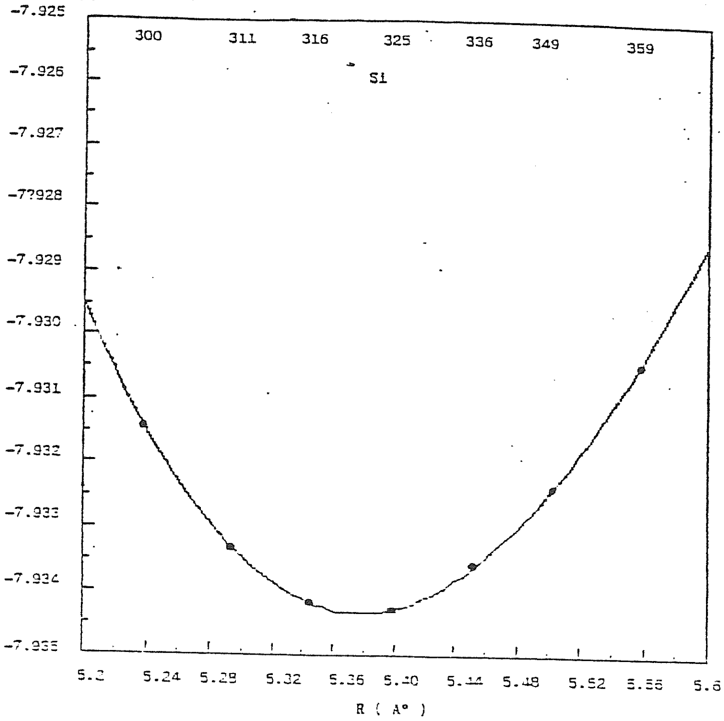

Figure 5. Total energy of Si calcalated as a function of a (points), curve is from a fit to Murnaghan' equation of state. Average number of PW s used at each a are shown at the top of the figure.

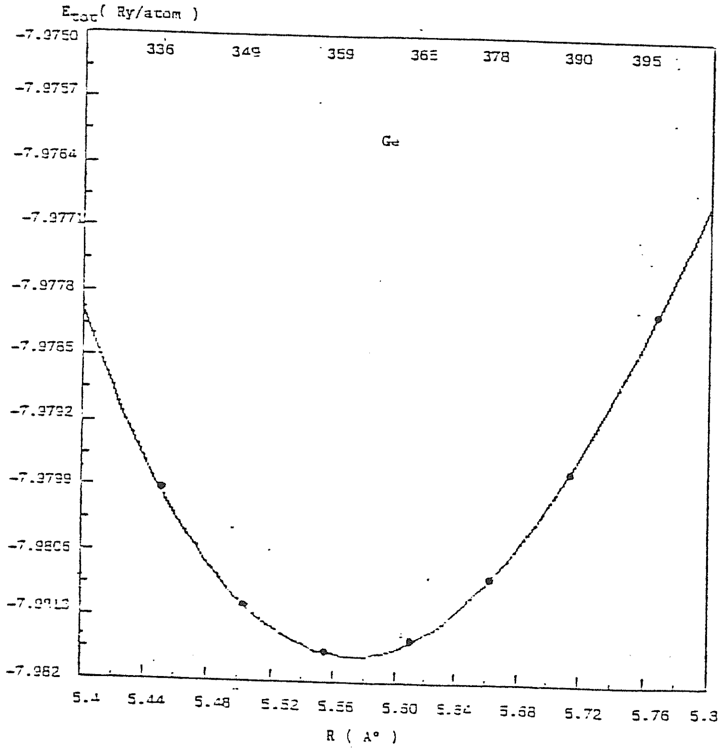

Figure 6. Total energy of Ge calculated as a function of a (points), curve is from a fit to Murnaghan' equation of state. Average number of PW s are shown at the top of the figure.

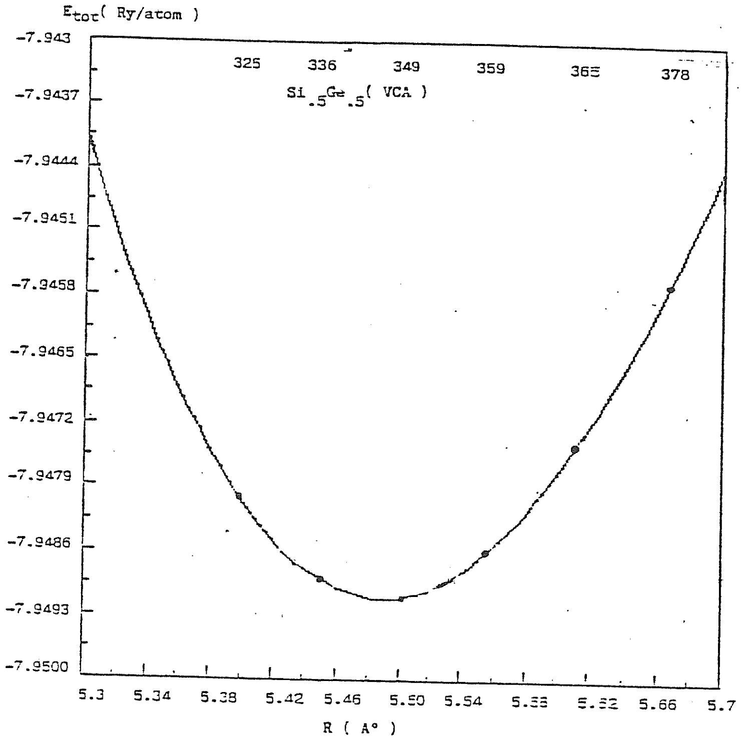

Figure 7. Total energy of $Si_{.5}Ge_{.5}$ alloys within VCA calculated as function of a (points), curve is from a fit to Murnaghan equation of state. Average number of PW s is shown et the top of the figure.

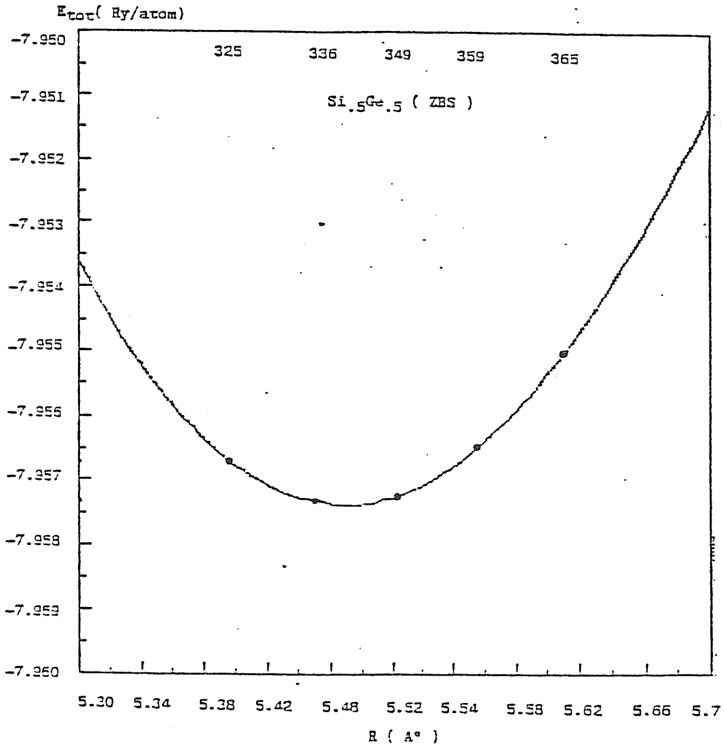

Figure 8. Total energy of $Si_{.5}Ge_{.5}$ alloys having ZBS calculated as function of a (points), curve is from a fit to Murnaghan equation of state . Average number of PW s are shown at the top of the figure.

V. Discussion.

The calculated minimum total energy of a mixture of Si and Ge with 50 at.% each is -7.95802Ry/atom, which is the average of the calculated values of pure Si and pure Ge. Comparing this value with the minimum total energies of $Si_{.5}Ge_{.5}$ alloys (see table (3)) within the VCA and having ZBS; we find that the mixture phase is more stable than both the phases of alloys considered here. The calculated total energy difference is 8.96 and 0.65 in mRy/atom in the case of the VCA and the ZBS, respectively. Our results are in qualitative agreement with the experimental result[15] : that the mixture phase is the stable one at $T = 0$. Contrary to previous theoretical results [17-18] we found that the ordered ZBS is more stable than the disordered phase within the VCA.

Experience has shown that there are theoretical uncertainties due to the use of different pseudopotentials, exchange and correlation energy expressions, cutoffs and the number of special points . This is the reason why we got smaller E_{tot}(min) for Ge than that for Si, contrary to the experimental and the calculated values of Yin and Cohen[9] (-7.8885 Ry/atom and -7.9086 Ry/atom for Ge and Si, respectively, using ten special points, 11.5 Ry constant energy cutoff and the Wigner expression to calculate the exchange and correlation energy). Since the E_{tot}(min) for Si calculated using Ceperly and Alder exchange and correlation energy is of order 10^{-2} Ry/atom greater than that calculated using the Wigner expression, and ten special points instead of two leads to a decrease in the E_{tot} of order of 10^{-3} Ry/atom[22]. One can argue that the discrepancy is mostly due to the different energy cutoffs and pseudopotentials used in the two works, and the pseudopotentials in particular in the case of Ge .

It is well known that within LDA one is able to reproduce the experimental lattice constant within 1 % (i.e., a deviation of a few hundredths of angestrom from the observed value). Since the deviation from Vegard's law is usually very small (a few thousandths of angestrom for $Si_{.5}Ge_{.5}$ alloys), it is meaningless to compare the theoretical lattice constants of the alloy phases with the value predicted by Vegard's law (the weighted average of lattice constants of pure materials) using the experimental lattice constants. Instead, it is much more meaningful to compare them with the value predicted using the theoretical lattice constants of pure materials. In such a way, our calculated deviation from Vegard's law is 0.015 Å and -0.006 Å in the case of $Si_{.5}Ge_{.5}$ alloys within the VCA and having the ZBS, respectively.

Experimentally (see the last two lines of table (3)) the deviation from Vegard's law (which is of interest in the alloys studies) is rather well predicted by the theory in the case of ZBS. While the large discrepancy in the case of VCA can serve as an indication that it is not a good model for these materials.

It should be mentioned that the structural disorder is completely neglected in this study. It has been pointed out by Zunger and Jaffe[30] that it plays an important rOle in the deviation of the energy-gaps from linearity (so-called energy-gap bowing), we expect it will be also important in studing other properties of alloys. This kind of disorder can be taken approximately into account by considering a large unit cell to allow for some structural disorder within it. The compositional disorder has been taken into account approximately using VCA, which is the best one that can be used in this theory.

This work will be extended by increasing the number of special points and the cutoff. However since, as explained above, we are more interested in the difference between the calculated values than in the absolute values, and in particular we are interested in the stability, we expect that the improvements will not have a relevent effect on the final result.

The energy band structure and the energy-gap bowing is an interesting subject, which we are presently studying

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