



**ISAS - INTERNATIONAL SCHOOL
FOR ADVANCED STUDIES**

**Structure and phase stability
of $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloy**

Thesis submitted for the degree of
"Magister Philosophiæ"

CANDIDATE

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October 1996

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SCUOLA INTERNAZIONALE SUPERIORE DI STUDI AVANZATI
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1 Introduction

Semiconductors are of relevant technological interest because of their wide use in the field of microelectronics. Nevertheless, the most used materials (group IV elements and group III-V compounds) allow a restricted range in the fundamental properties such as energy gap, lattice parameter and electron mobility.

It is possible to overcome these limitations using solid solutions $A_x B_{1-x}$, obtaining intermediate properties between components A and B. As a consequence, the knowledge of the relative stability of such alloys as a function of temperature and concentration with respect to the component segregation results to be of fundamental importance.

The thermodynamical "driving force" at the usual experimental conditions of constant temperature and pressure is the Gibbs free energy $G(P,T)=E+PV-TS$. From a statistical point of view, the thermodynamical properties can be obtained by the evaluation of Boltzmann integrals in phase space for a macroscopic sample.

From the computational point of view, the evaluation of these Boltzmann averages cannot be performed exactly because the number of possible configurations is enormous for any system large enough to be statistically representative of a macroscopic system.

Standard MonteCarlo techniques [1] are then used to sample the phase space with a Boltzmann distribution and the Gibbs free energy is computed using the thermodynamical integration [2] .

The major problem concerning the MonteCarlo sampling in connection with First Principle Calculations is that the energy of hundreds of configurations are needed for each average calculation and although Density Functional Theory (DFT) [3] has proved to be a succesful approach for what concerns crystal energetics , the computational time and resources needed are proportional to the cube of the number of inequivalent atoms present in the crystal.

Calculations for a thousand inequivalent atoms are nowadays still prohibitive. Nevertheless, the introduction of a new and more profitable approach to the theory of perturbations [4] in the field of the density functional has allowed the study of structural [5], dielectric [6] and vibrational [7] properties otherwise untreatable with conventional methods.

Following this approach, the presence of substitutional disorder between atoms very similar from a chimical point of view suggests to treat each configuration of the system as a little perturbation to a reference system (the “virtual crystal”), composed by atoms with intermediate properties between those of the true costituents, such that the perturbation transforms the virtual atoms in real atoms of the considered type. The reference system will have complete transitional simmetry and can be easily studied with the usual methods. With this alchemical trick it is possible to reformulate our original problem using a proper expansion of the energy in suitable configurational variables, so that it formally maps into

an Ising spin model with many neighbour interactions.

So, at this point, the only source of error with respect to the complete DFT calculations is due to the truncation in the energy expansion at some finite term. We obviously expect that the inclusion of more terms will reduce the error of our approximation.

All the previous studies of this kind ([9] for $\text{Si}_x\text{Ge}_{1-x}$, [10] for $\text{Ga}_x\text{In}_{1-x}\text{P}$, [11] for $\text{Ga}_x\text{Al}_{1-x}\text{As}$ and others), have stopped the energy expansion at 2nd order, obtaining a general agreement with the experimental results.

In the present work we try to introduce the third order terms in the energy expansion of $\text{Ga}_x\text{In}_{1-x}\text{P}$ to improve the energetics and phase diagram predictions of that particular system, but also with the aim of developing a strategy for taking into account in some easy way the very complicated third order contributions, where these can be of significant importance.

1.1 Plan of the work

In chapter 2 the perturbative approach for the calculation of the configurational energy is presented ; the formalism is developed up to the third order in the expansion.

In chapter 3 we check the reliability of our perturbative expansion comparing the results so obtained for some superlattices with the self consistent calculations performed for the

same structures. In this way we can evaluate the different accuracy achieved truncating the expansion at different orders.

Chapter 4 is devoted to the presentation of the phase diagrams obtained using the MonteCarlo techniques. We can appreciate the thermodynamical effect of the inclusion of the third order terms in the energy expansion by comparing the phase diagrams obtained with and without their inclusion .

2 Semiconductor alloy: energy expansion

In the last years, *ab initio* theoretical calculations of the energetics of crystal systems have been performed with great success in the framework of density functional theory (DFT). These calculations are performed at zero temperature, where the properties of interest can be obtained from the determination of the electronic ground state.

It is obviously impossible to solve exactly the many-body Schrödinger equations of electrons and nuclei in a crystal, but an approximation universally used in solid state physics, known as the Born-Oppenheimer approximation, allows to decouple the “fast” electronic variables from the “slow” ionic ones, by virtue of the great difference of masses. The system is thus divided in two subsystems: the electrons move in the potential of the fixed nuclei, following adiabatically their slow motion and remaining always close to the quantum-mechanical ground state, while the ions are treated as if they were classical particles in the effective potential determined by the electronic ground state.

In the spirit of this approximation, it is possible to simplify the problem, and DFT provides the appropriate mathematical scheme for determining self-consistently the ground

state of the whole system.

Nevertheless, for large cells of the order of one thousand atoms the computational time requested is such long that this technique results to be unsuitable for our present case, in which many tens thousands energy calculations are necessary for each temperature.

What we can do is to take DFT as a starting point for further approximations. The study of alloys with substitutional disorder of atoms with similar chemical properties leads to face the energetics problem with a perturbative approach, treating the real system as the result of a little variation with respect to an intermediate virtual crystal. The energy expansion is then truncated, retaining the few lowest order terms.

2.1 Density functional theory

This theory was developed 30 years ago on the basis of the Hohenberg-Kohn theorem [3], which proves the uniqueness of the external potential acting on the subsystem of the electrons as a functional of the electronic density $n(\mathbf{r})$. The energy of the electrons can be written as

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r}, \quad (2.1)$$

where $F[n]$ is a universal functional of the electronic density (independent on the external potential), and $V(\mathbf{r})$ is the “external” potential (with respect to the electrons) generated by the ionic cores.

In principle this problem should be solved via the constrained minimization of this functional, in general unknown, with respect to the electron density, that must always be

normalized to the number N of electrons:

$$\int n(\mathbf{r})d\mathbf{r} = N. \quad (2.2)$$

In order to apply this theory to actual calculations, Kohn and Sham proposed to separate the functional $F[n]$ into three distinct contributes:

$$F[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})]. \quad (2.3)$$

$T_0[n(\mathbf{r})]$ is the kinetic energy of a system of noninteracting electrons of density $n(\mathbf{r})$, the second is the classical Hartree term describing the Coulomb potential of the electrons, while $E_{xc}[n(\mathbf{r})]$, defined by this formula, is known as the exchange and correlation energy and contains all the information about the many-body interactions among electrons that we do not know.

This way, the problem of constrained minimization becomes the problem of solving a set of self-consistent single particle equations:

$$\underbrace{\left[-\frac{\nabla^2}{2} + V_{SCF}(\mathbf{r}) \right]}_{H_{KS}} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.4)$$

$$V_{SCF}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[n(\mathbf{r})] \quad (2.5)$$

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \theta(\epsilon_i - \epsilon_F). \quad (2.6)$$

These are the well known Kohn-Sham (KS) equations [8], where the Fermi energy ϵ_F is defined by the constraint on the number of electrons, $v_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r})$ is the exchange-correlation potential and the single particle orbitals satisfy the orthonormality constraint $\int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$.

The Kohn-Sham equations are exact and still contain a completely unknown term in the exchange- correlation potential . In order to face this problem it is necessary, at this point, to introduce some approximations. A very natural approximation to DFT is the well-known local density approximation (LDA), in which the exchange-correlation energy is taken as a local *function* rather than a functional of the density:

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad (2.7)$$

and the potential is given by:

$$v_{xc}(\mathbf{r}) = \frac{d}{dn}(n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))) = \mu_{xc}(n(\mathbf{r})). \quad (2.8)$$

In this approximation, the total energy of the crystal in its electronic ground state is:

$$\begin{aligned} E^{tot} &= -\sum_i \theta(\epsilon_i - \epsilon_F) \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} + \int V_{ion} n(\mathbf{r}) d\mathbf{r} \\ &+ \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r})) d\mathbf{r} \\ &+ \sum_{\mathbf{R},s,s'}' \frac{Z_s Z_{s'}}{|\mathbf{R} + \tau_s - \tau_{s'}|}. \end{aligned} \quad (2.9)$$

LDA works surprisingly well for a large variety of systems, even more than any possible expectations, but it is known to be worse when describing weak atomic bondings. In the last decade, a lot of improvements to LDA were proposed [12, 13, 14, 15], but none of them seems to be a real “breakthrough” in this direction.

They are mostly based on the inclusion, in the dependence of the exchange and correlation functional, not only of the electronic density, but also of its gradient, and even of the Laplacian. For this reason they are commonly known as gradient-correction approximations

(GGA). These kinds of new functionals are not fully satisfactory from a theoretical point of view, but certainly are able to describe better those situations in which LDA breaks down.

2.1.1 The plane-wave pseudopotential method

The actual solution of the KS equations can be obtained expanding the KS wavefunctions on a basis set. The most widely used choice of this basis is that of plane waves (PW), which have the great advantage of being translationally invariant:

$$\psi_i(\mathbf{r}) = \psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} c_n(\mathbf{k} + \mathbf{G}) \quad (2.10)$$

where \mathbf{k} belongs to the first Brillouin Zone (BZ) of the crystal, \mathbf{G} is a reciprocal lattice vector and n is the band index. The PW basis set is infinite and it is usually truncated by choosing a kinetic energy cutoff through the condition:

$$|\mathbf{k} + \mathbf{G}|^2 \leq E_{cut}. \quad (2.11)$$

To treat explicitly all the electrons it would be necessary to choose a very large number of PW in order to describe accurately their rapid oscillations near the nucleus. This would require a very heavy computational effort for the calculation. It is possible to avoid this problem freezing the core electrons in the atomic configuration around the ions, and considering only the valence electrons.

To do this, one introduces the *pseudopotentials*, able to describe the interactions between these electrons and the *pseudoions* (ions+ core electrons). The valence electrons wavefunctions are considerably smoother near the nucleus, but are identical to the “true”

wavefunctions outside the core region. This method is now well-established in computational physics, and the results are very accurate.

The widely-used norm-conserving pseudopotentials [16] consist of a local contribution for the radial function and a non-local one for the angular part:

$$v_s(\mathbf{r}, \mathbf{r}') = v_s^{loc}(r)\delta(\mathbf{r} - \mathbf{r}') + \sum_{l=0}^{l_{max}} v_{s,l}(r)\delta(r - r')P_l(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \quad (2.12)$$

where P_l is the projector on the angular momentum l .

This form of *semilocal* pseudopotential still is not the most convenient one from a computational point of view, and for this reason Kleinman and Bylander (KB) introduced [17] a fully non-local pseudopotential in which also the radial part of the potential is non-local:

$$v_s^{(NL)}(\mathbf{r}, \mathbf{r}') = v_s^{loc}(r)\delta(\mathbf{r} - \mathbf{r}') + \sum_{l=0}^{l_{max}} v_{s,l}^{(NL)}(\mathbf{r}, \mathbf{r}'), \quad (2.13)$$

where

$$v_{s,l}^{(NL)}(\mathbf{r}, \mathbf{r}') = \sum_{m=-l}^l \frac{v_{s,l}(r)R_{s,l}(r)Y_l^m(\theta, \phi)Y_l^{*m}(\theta', \phi')R_{s,l}(r')v_{s,l}(r')}{\langle R_{s,l}|v_{s,l}|R_{s,l} \rangle}. \quad (2.14)$$

This form of the potential allows a very convenient simplification of its matrix elements in reciprocal space, where the KS equations are iteratively solved.

The only problem which one is often compelled to face (this is in fact our case) with the KB form of pseudopotentials is that of “ghosts”. The non-local character of the KB potential makes possible that eigenstates with nodes have lower eigenvalues than the zero-node state [18]. However there is a standard way of eliminating this problem, simply by collecting together in a different manner all the l -different contributes to the potential.

2.2 Computational alchemy

The fundamental difficulty to treat disordered crystals is due to the lack of translational symmetry of the system, so that it is not possible to extract the bulk properties from the study of the primitive cell, as it is in ordered crystals.

That's why we try to separate the energy of a disordered alloy as a sum of two contributions: the first contribution is given by the energy of a virtual system with full translational symmetry; the second contribution is considered as a result of a perturbation to the virtual crystal.

First of all, let's consider a substitutional binary alloy A_xB_{1-x} , neglecting atomic relaxation with respect to ideal lattice positions. A general microscopic configuration C is completely defined by a set of spin-like variables $\sigma_{\mathbf{R}}$ taking values $+1$ or -1 if atom in site \mathbf{R} is of type A or B respectively. The total potential produced by such a configuration of atoms can be written as:

$$V_{est}(\mathbf{r}) = \sum_{\mathbf{R}} \left(\frac{1 + \sigma_{\mathbf{R}}}{2} v_A(\mathbf{r} - \mathbf{R}) + \frac{1 - \sigma_{\mathbf{R}}}{2} v_B(\mathbf{r} - \mathbf{R}) \right) \quad (2.15)$$

where v_A and v_B are the respective atomic pseudopotentials.

The preceding expression can be recast in the form:

$$\begin{aligned} V_{est}(\mathbf{r}) &= \underbrace{\sum_{\mathbf{R}} \frac{1}{2} (v_A(\mathbf{r} - \mathbf{R}) + v_B(\mathbf{r} - \mathbf{R}))}_{V_o} + \underbrace{\sum_{\mathbf{R}} \sigma_{\mathbf{R}} \frac{1}{2} (v_A(\mathbf{r} - \mathbf{R}) - v_B(\mathbf{r} - \mathbf{R}))}_{\Delta V(\mathbf{r})} \\ &= V_o + \Delta V(\mathbf{r}) \end{aligned} \quad (2.16)$$

where

$$\Delta V(\mathbf{r}) = \sum_{\mathbf{R}} \sigma_{\mathbf{R}} \Delta v(\mathbf{r} - \mathbf{R}) \quad (2.17)$$

Eq (2.16) shows that the electronic potential can be considered as a superposition of a mean configurational independent potential $V_o(\mathbf{r})$ with a configurational modulation $\sum_{\mathbf{R}} \sigma_{\mathbf{R}} \Delta v(\mathbf{r} - \mathbf{R})$.

In general, the ground state energy variation to a perturbation can be obtained from the electron density variation. Let's consider a system described by the hamiltonian $H = T + V_{\lambda}$, where V_{λ} is a potential depending on parameters $\lambda \equiv \{\lambda_i\}$ and $E_{\lambda} = \langle \psi_{\lambda} | H_{\lambda} | \psi_{\lambda} \rangle$ is the respective ground state energy. From Hellman-Feynman [19] theorem we have:

$$\frac{\partial E_{\lambda}}{\partial \lambda_i} = \langle \psi_{\lambda} | \frac{\partial H_{\lambda}}{\partial \lambda_i} | \psi_{\lambda} \rangle = \int n_{\lambda}(\mathbf{r}) \frac{\partial V_{\lambda}}{\partial \lambda_i} d\mathbf{r} \quad (2.18)$$

Expanding the λ -dependent r.h.s. quantities around $\lambda = 0$ and integrating with respect to λ_i , we obtain:

$$\begin{aligned} E_{\lambda} &= E_o + \sum_i \lambda_i \int n_o(\mathbf{r}) \left. \frac{\partial V_{\lambda}}{\partial \lambda_i} \right|_o d\mathbf{r} \\ &+ \frac{1}{2} \sum_{i,j} \lambda_i \lambda_j \int \left(\left. \frac{\partial n_{\lambda}(\mathbf{r})}{\partial \lambda_j} \right|_o \left. \frac{\partial V_{\lambda}}{\partial \lambda_i} \right|_o + n_o(\mathbf{r}) \left. \frac{\partial^2 V_{\lambda}}{\partial \lambda_i \partial \lambda_j} \right|_o \right) d\mathbf{r} + \mathbf{O}(\lambda^3) + \dots \end{aligned} \quad (2.19)$$

The linear response of the system to a perturbation can be calculated using Density Functional Perturbation Theory (DFPT) [4]. A variation ΔV_{ext} in the external potential V_{ext} modifies as a consequence the selfconsistent potential V_{SCF} ; up to linear order Kohn-Sham equations for the charge density response become:

$$\left[-\nabla^2 + V_{SCF}(\mathbf{r}) - \varepsilon_i \right] \Delta \phi_i(\mathbf{r}) = -(\Delta V_{SCF}(\mathbf{r}) - \langle \phi_i | \Delta V_{SCF} | \phi_i \rangle) \phi_i(\mathbf{r})$$

$$\Delta V_{SCF}(\mathbf{r}) = \Delta V_{ext}(\mathbf{r}) + 2 \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{d\mu_{xc}}{dn}(n_o(\mathbf{r})) \Delta n(\mathbf{r})$$

$$\Delta n(\mathbf{r}) = 2 \sum_i \phi_i^*(\mathbf{r}) \Delta \phi_i(\mathbf{r}) \theta(\varepsilon_{Fermi} - \varepsilon_i) \quad (2.20)$$

It is important to note the fundamental role of symmetry when we use these expressions in reciprocal space: it is a general rule that a perturbation belonging to a definite irriducible representation of the symmetry group of the system induces a linear response of the same irriducible representation of the perturbation. This means that, in a periodic crystal, a perturbation of definite \mathbf{q} induces a linear response of the same periodicity. In this way, perturbations of arbitrary \mathbf{q} can be computed from the solution of the linear system (2.20) in its reciprocal space formulation, with the same complexity of the original problem without the use of real space supercells.

As previously seen, the alloy is described by an external potential

$$V_{ext}(\mathbf{r}) = V_o(\mathbf{r}) + \Delta V(\mathbf{r}) = V_o(\mathbf{r}) + \sum_{\mathbf{R}} \sigma_{\mathbf{R}} \Delta v(\mathbf{r} - \mathbf{R}) \quad (2.21)$$

So we can consider $\sigma_{\mathbf{R}_s}$ as continuous variables which transform all virtual atoms in each site in real atoms going from 0 to ± 1 . Identifying $\{\lambda_i\}$ with $\{\sigma_{\mathbf{R}_s}\}$ and V_λ with $V_{ext}(\mathbf{r})$, eq.(2.19) gives:

$$E\{\sigma\} = E_o + \sum_{\mathbf{R}_s} K_s \sigma_{\mathbf{R}_s} + \sum_{\mathbf{R}\mathbf{R}'} \left[\frac{1}{2} \sum_s \sum_{s'} J_{ss'}(\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'_{s'}} \right] +$$

$$+ \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{3!} \sum_{ss's''} L_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}s} \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right] + \dots \quad (2.22)$$

where

$$K_s = \left. \frac{\partial E}{\partial \sigma_{\mathbf{R}s}} \right|_0 = \int \Delta v(\mathbf{r}) n_o(\mathbf{r}) d\mathbf{r} \quad (2.23)$$

$$J_{ss'}(\mathbf{R} - \mathbf{R}') = \left. \frac{\partial^2 E}{\partial \sigma_{\mathbf{R}s} \partial \sigma_{\mathbf{R}'s'}} \right|_0 = \int \Delta V_{\sigma_{\mathbf{R}s}}(\mathbf{r} - \mathbf{R}) \Delta n_{\sigma_{\mathbf{R}'s'}}(\mathbf{r} - \mathbf{R}') d\mathbf{r} \quad (2.24)$$

$$L_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') = \left. \frac{\partial^3 E}{\partial \sigma_{\mathbf{R}s} \partial \sigma_{\mathbf{R}'s'} \partial \sigma_{\mathbf{R}''s''}} \right|_0 \quad (2.25)$$

All these ingredients can be computed from the knowledge of the linear response $\Delta n_{\sigma_{\mathbf{R}'s'}}$. For the third order derivative this is guaranteed by the 2n+1 theorem [20][21] stating that the knowledge of the n^{th} density derivatives are enough to calculate up to the $(2n+1)^{th}$ derivatives of the energy.

2.2.1 Including atomic relaxation

Up to now we have imagined to take a reference unexisting system and transform its virtual atoms into real ones. But this is not enough to obtain a real system, because real atoms tends to relax from such ideal positions, in order to accomodate the chemical bonds with their neighbours, depending on the particular configuration $\{\sigma\}$ which is realized. For taking into account atomic relaxation, we introduce atomic displacements $\{\mathbf{U}\}$ and we expand the

energy of the virtual crystal (for which $\{\sigma\}$ and $\{\mathbf{U}\}$ are zero) with respect to both chemical perturbations and atomic displacements. Thus we obtain:

$$\begin{aligned}
E\{\mathbf{U}, \sigma\} &= E_0 + \sum_{\mathbf{R}_s} K_s \sigma_{\mathbf{R}_s} + \\
&+ \sum_{\mathbf{R}\mathbf{R}'} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s'\alpha'} C_{ss'}^{\alpha\alpha'}(\mathbf{R} - \mathbf{R}') U_{\mathbf{R}_s}^\alpha U_{\mathbf{R}'s'}^{\alpha'} - \sum_{s\alpha} \sum_{s'\alpha'} F_{ss'}^\alpha(\mathbf{R} - \mathbf{R}') U_{\mathbf{R}_s}^\alpha \sigma_{\mathbf{R}'s'} + \frac{1}{2} \sum_s \sum_{s'} J_{ss'}(\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'s'} \right] \\
&+ \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{3!} \sum_{s\alpha} \sum_{s'\alpha'} \sum_{s''\alpha''} \Phi_{ss's''}^{(1)}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') U_{\mathbf{R}_s}^\alpha U_{\mathbf{R}'s'}^{\alpha'} U_{\mathbf{R}''s''}^{\alpha''} \right] \\
&+ \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s'\alpha'} \sum_{s''\alpha''} F_{ss's''}^{(1)}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') U_{\mathbf{R}_s}^\alpha U_{\mathbf{R}'s'}^{\alpha'} \sigma_{\mathbf{R}''s''} \right] \\
&+ \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s's''} J_{ss''}^{(1)}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') U_{\mathbf{R}_s}^\alpha \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right] \\
&+ \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{3!} \sum_{ss's''} L_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right]
\end{aligned} \tag{2.26}$$

where the new coefficients which appear in this global expansion are:

$$C_{ss'}^{\alpha\alpha'}(\mathbf{R} - \mathbf{R}') = \left. \frac{\partial^2 E}{\partial U_{\mathbf{R}_s}^\alpha \partial U_{\mathbf{R}'s'}^{\alpha'}} \right|_0 = \int \Delta V_{U_{\mathbf{R}_s}^\alpha}(\mathbf{r} - \mathbf{R}) \Delta n_{U_{\mathbf{R}'s'}^{\alpha'}}(\mathbf{r} - \mathbf{R}') d\mathbf{r} \tag{2.27}$$

$$F_{ss'}^\alpha(\mathbf{R} - \mathbf{R}') = - \left. \frac{\partial^2 E}{\partial U_{\mathbf{R}_s}^\alpha \partial \sigma_{\mathbf{R}'s'}} \right|_0 = - \int \Delta V_{U_{\mathbf{R}_s}^\alpha}(\mathbf{r} - \mathbf{R}) \Delta n_{\sigma_{\mathbf{R}'s'}}(\mathbf{r} - \mathbf{R}') d\mathbf{r} \tag{2.28}$$

$$\Phi_{ss's''}^{(1)}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') = \left. \frac{\partial^3 E}{\partial U_{\mathbf{R}_s}^\alpha \partial U_{\mathbf{R}'s'}^{\alpha'} \partial U_{\mathbf{R}''s''}^{\alpha''}} \right|_0 \tag{2.29}$$

$$F_{ss's''}^{(1)}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') = \left. \frac{\partial^3 E}{\partial U_{\mathbf{R}_s}^\alpha \partial U_{\mathbf{R}'s'}^{\alpha'} \partial \sigma_{\mathbf{R}''s''}} \right|_0 \tag{2.30}$$

$$J_{\alpha s s' s''}^{(1)}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') = \left. \frac{\partial^3 E}{\partial U_{\mathbf{R}_s}^\alpha \partial \sigma_{\mathbf{R}' s'} \partial \sigma_{\mathbf{R}'' s''}} \right|_0 \quad (2.31)$$

Up to now \mathbf{U}, σ are independent variables. Since for the virtual crystal we have:

$$\left. \frac{\partial E}{\partial U_{\mathbf{R}_s}^\alpha} \right|_0 = 0 \quad (2.32)$$

this vanishing term has been omitted in the expansion.

What we want to do now is to define another function $\tilde{E}\{\sigma\}$ from $E\{\mathbf{U}, \sigma\}$. Let :

$$\tilde{E}\{\sigma\} = \min_{\mathbf{U}} E\{\mathbf{U}, \sigma\} = E\{\mathbf{U}(\sigma), \sigma\} \quad (2.33)$$

where $\{\mathbf{U}(\sigma)\}$ are determined from the equation:

$$\left. \frac{\partial E}{\partial U_{\mathbf{R}_s}^\alpha} \right|_{\{\mathbf{U}, \sigma\}} = 0 \quad \forall \mathbf{R}_s \alpha \quad (2.34)$$

Now we can expand $\tilde{E}\{\sigma\}$:

$$\begin{aligned} \tilde{E}\{\sigma\} = & \tilde{E}_0 + \sum_{\mathbf{R}_s} \tilde{K}_s \sigma_{\mathbf{R}_s} + \sum_{\mathbf{R}\mathbf{R}'} \left[\frac{1}{2} \sum_s \sum_{s'} \tilde{J}_{ss'} (\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}' s'} \right] + \\ & + \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{3!} \sum_{ss's''} \tilde{L}_{ss's''} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}' s'} \sigma_{\mathbf{R}'' s''} \right] + \dots \end{aligned} \quad (2.35)$$

We want to find out the relationships between these coefficients and those obtained for the expansion of $E\{\mathbf{U}, \sigma\}$. To do that, we just need to substitute in (2.26) the σ expansion of $\mathbf{U}_{\mathbf{R}_s}$, which is:

$$U_{\mathbf{R}_s}^\alpha(\sigma) = \sum_{\mathbf{R}'s'} \frac{\partial U_{\mathbf{R}_s}^\alpha}{\partial \sigma_{\mathbf{R}'s'}} \Big|_0 \sigma_{\mathbf{R}'s'} + \frac{1}{2} \sum_{\mathbf{R}'\mathbf{R}''} \sum_{s's''} \frac{\partial^2 U_{\mathbf{R}_s}^\alpha}{\partial \sigma_{\mathbf{R}'s'} \partial \sigma_{\mathbf{R}''s''}} \Big|_0 \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} + \dots \quad (2.36)$$

(note that in this expansion we have supposed that $U_{\mathbf{R}_s}^\alpha(\sigma = \mathbf{0}) = 0$, as it is if for $\{\sigma\} = 0$ the configuration $\{\mathbf{U}\} = 0$ corresponds to a minimum, which we previously expressed by eq. (2.32)).

The coefficients which appear in this expansion can be found directly from eq.(2.34) using eq.(2.26):

$$\begin{aligned} 0 = \frac{\partial E}{\partial U_{\mathbf{R}_s}^\alpha} \Big|_{\{\mathbf{U}, \sigma\}} &= \sum_{\mathbf{R}'} \left[\sum_{s'\alpha'} C_{ss'}^{\alpha\alpha'} (\mathbf{R} - \mathbf{R}') U_{\mathbf{R}'s'}^{\alpha'} - \sum_{s'} F_{ss'}^\alpha (\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}'s'} \right] + \\ &\sum_{\mathbf{R}'\mathbf{R}''} \left[\frac{1}{2} \sum_{s'\alpha'} \sum_{s''\alpha''} \Phi_{ss's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') U_{\mathbf{R}'s'}^{\alpha'} U_{\mathbf{R}''s''}^{\alpha''} \right] + \\ &\sum_{\mathbf{R}'\mathbf{R}''} \left[\sum_{s'\alpha'} \sum_{s''} F_{ss's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') U_{\mathbf{R}'s'}^{\alpha'} \sigma_{\mathbf{R}''s''} \right] + \\ &\sum_{\mathbf{R}'\mathbf{R}''} \left[\frac{1}{2} \sum_{s's''} J_{ss's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right] + \dots \end{aligned} \quad (2.37)$$

Multiplying by $C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1}$, summing over \mathbf{R}_s, α and isolating the resulting $U_{\bar{\mathbf{R}}\bar{s}}^{\bar{\alpha}}$

yields:

$$\begin{aligned} U_{\bar{\mathbf{R}}\bar{s}}^{\bar{\alpha}} &= \sum_{\mathbf{R}\mathbf{R}'} \left[\sum_{s\alpha} \sum_{s'} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} F_{ss'}^\alpha (\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}'s'} \right] - \\ &- \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s'\alpha'} \sum_{s''\alpha''} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} \Phi_{ss's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') U_{\mathbf{R}'s'}^{\alpha'} U_{\mathbf{R}''s''}^{\alpha''} \right] \\ &- \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\sum_{s\alpha} \sum_{s'\alpha'} \sum_{s''} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} F_{ss's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') U_{\mathbf{R}'s'}^{\alpha'} \sigma_{\mathbf{R}''s''} \right] \\ &- \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s's''} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} J_{ss's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right] - \dots \end{aligned} \quad (2.38)$$

Now, substituting each appearance of $U_{\mathbf{R}_s}^{\bar{\alpha}}(\sigma)$ at r.h.s. of eq.(2.38) with eq.(2.36) and comparing with eq.(2.36), we obtain the coefficients of eq.(2.36) in terms of the coefficients in eq.(2.26).

At first order we have:

$$U_{\mathbf{R}_s}^{\bar{\alpha}}(1) = \sum_{\mathbf{R}'s'} \left. \frac{\partial U_{\mathbf{R}_s}^{\bar{\alpha}}}{\partial \sigma_{\mathbf{R}'s'}} \right|_0 \sigma_{\mathbf{R}'s'} = \sum_{\mathbf{R}\mathbf{R}'} \left[\sum_{s\alpha} \sum_{s'} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} F_{ss'}^{\alpha} (\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}'s'} \right] \quad (2.39)$$

which yields:

$$\left. \frac{\partial U_{\mathbf{R}_s}^{\bar{\alpha}}}{\partial \sigma_{\mathbf{R}'s'}} \right|_0 = \sum_{\mathbf{R}} \sum_{s\alpha} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} F_{ss'}^{\alpha} (\mathbf{R} - \mathbf{R}') \quad (2.40)$$

At second order:

$$\begin{aligned} U_{\mathbf{R}_s}^{\bar{\alpha}}(2) &= \frac{1}{2} \sum_{\mathbf{R}'\mathbf{R}''} \sum_{s's''} \left. \frac{\partial^2 U_{\mathbf{R}_s}^{\bar{\alpha}}}{\partial \sigma_{\mathbf{R}'s'} \partial \sigma_{\mathbf{R}''s''}} \right|_0 \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} = \\ &- \frac{1}{2} \sum_{\mathbf{R}'\mathbf{R}''} \sum_{s's''} \left[\sum_{\mathbf{R}\mathbf{T}'\mathbf{T}''} \sum_{s\alpha} \sum_{d'\beta'} \sum_{d''\beta''} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} \Phi_{\alpha\beta'\beta''}^{(1)}(s'd'd'') (\mathbf{R} - \mathbf{T}'', \mathbf{T}' - \mathbf{T}'') \left. \frac{\partial U_{\mathbf{T}'d'}^{\beta'} \right|_0 \left. \frac{\partial U_{\mathbf{T}''d''}^{\beta''} \right|_0 \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right] \\ &- \sum_{\mathbf{R}'\mathbf{R}''} \sum_{s's''} \left[\sum_{\mathbf{R}\mathbf{T}'} \sum_{s\alpha} \sum_{d'\beta'} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} F_{sd's''}^{(1)\alpha\beta'} (\mathbf{R} - \mathbf{R}'', \mathbf{T}' - \mathbf{R}'') \left. \frac{\partial U_{\mathbf{T}'d'}^{\beta'} \right|_0 \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right] \\ &- \frac{1}{2} \sum_{\mathbf{R}'\mathbf{R}''} \sum_{s's''} \left[\sum_{\mathbf{R}} \sum_{s\alpha} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} J_{\alpha s's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \right] \end{aligned} \quad (2.41)$$

so that, imposing invariance symmetry in the order of derivation:

$$\begin{aligned}
\left. \frac{\partial^2 U_{\mathbf{R}_s}^\alpha}{\partial \sigma_{\mathbf{R}'s'} \partial \sigma_{\mathbf{R}''s''}} \right|_0 &= - \sum_{\mathbf{R}} \sum_{s\alpha} C_{\bar{s}s}^{\bar{\alpha}\alpha} (\bar{\mathbf{R}} - \mathbf{R})^{-1} \left\{ J_{\alpha s's''}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') + \right. \\
&+ \sum_{\mathbf{T}'\mathbf{T}''} \sum_{d'\beta'} \sum_{d''\beta''} \Phi_{s'd'd''}^{(1)} (\mathbf{R} - \mathbf{T}'', \mathbf{T}' - \mathbf{T}'') \left. \frac{\partial U_{\mathbf{T}'d'}^{\beta'} \right|_0}{\partial \sigma_{\mathbf{R}'s'}} \frac{\partial U_{\mathbf{T}''d''}^{\beta''} \right|_0}{\partial \sigma_{\mathbf{R}''s''}} + \\
&+ \sum_{\mathbf{T}'} \sum_{d'\beta'} \left[F_{\alpha\beta'}^{(1)} (\mathbf{R} - \mathbf{R}'', \mathbf{T}' - \mathbf{R}'') \frac{\partial U_{\mathbf{T}'d'}^{\beta'} \right|_0}{\partial \sigma_{\mathbf{R}'s'}} + F_{\alpha\beta'}^{(1)} (\mathbf{R} - \mathbf{R}', \mathbf{T}' - \mathbf{R}') \frac{\partial U_{\mathbf{T}'d'}^{\beta'} \right|_0}{\partial \sigma_{\mathbf{R}''s''}} \right] \left. \right\} \quad (2.42)
\end{aligned}$$

which we can further explicit by substitution of expression (2.40). Now we are ready to put eq.(2.36) in eq.(2.26). This immediately yields:

$$\tilde{E}_o = E_o \quad (2.43)$$

$$\tilde{K}_s = K_s \quad (2.44)$$

Let's find $\tilde{J}_{ss'} (\mathbf{R} - \mathbf{R}')$:

$$\begin{aligned}
\frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \sum_{ss'} \tilde{J}_{ss'} (\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'s'} &= \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \sum_{ss'} J_{ss'} (\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'s'} + \\
\frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \sum_{ss'} \sum_{\mathbf{T}\mathbf{T}'} \sum_{d\alpha} \sum_{d'\alpha'} C_{dd'}^{\alpha\alpha'} (\mathbf{T} - \mathbf{T}') \frac{\partial U_{\mathbf{T}d}^\alpha \right|_0}{\partial \sigma_{\mathbf{R}_s}} \frac{\partial U_{\mathbf{T}'d'}^{\alpha'} \right|_0}{\partial \sigma_{\mathbf{R}'s'}} &\sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'s'} - \sum_{\mathbf{R}\mathbf{R}'} \sum_{ss'} \sum_{\mathbf{T}} \sum_{d\alpha} F_{ds'}^\alpha (\mathbf{T} - \mathbf{R}') \frac{\partial U_{\mathbf{T}d}^\alpha \right|_0}{\partial \sigma_{\mathbf{R}_s}} \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'s'} \quad (2.45)
\end{aligned}$$

so that:

$$\begin{aligned}
\tilde{J}_{ss'} (\mathbf{R} - \mathbf{R}') &= J_{ss'} (\mathbf{R} - \mathbf{R}') + \sum_{\mathbf{T}\mathbf{T}'} \sum_{d\alpha} \sum_{d'\alpha'} C_{dd'}^{\alpha\alpha'} (\mathbf{T} - \mathbf{T}') \frac{\partial U_{\mathbf{T}d}^\alpha \right|_0}{\partial \sigma_{\mathbf{R}_s}} \frac{\partial U_{\mathbf{T}'d'}^{\alpha'} \right|_0}{\partial \sigma_{\mathbf{R}'s'}} - \\
&- \sum_{\mathbf{T}} \sum_{d\alpha} \left\{ F_{ds'}^\alpha (\mathbf{T} - \mathbf{R}') \frac{\partial U_{\mathbf{T}d}^\alpha \right|_0}{\partial \sigma_{\mathbf{R}_s}} + F_{ds}^\alpha (\mathbf{T} - \mathbf{R}) \frac{\partial U_{\mathbf{T}d}^\alpha \right|_0}{\partial \sigma_{\mathbf{R}'s'}} \right\} \quad (2.46)
\end{aligned}$$

Substituting expression (2.40) and rearranging, we have:

$$\tilde{J}_{ss'}(\mathbf{R} - \mathbf{R}') = J_{ss'}(\mathbf{R} - \mathbf{R}') - \sum_{\mathbf{T}\mathbf{R}''} \sum_{d\alpha} \sum_{s''\beta} F_{ds'}^\alpha(\mathbf{T} - \mathbf{R}') C_{ds''}^{\alpha\beta}(\mathbf{T} - \mathbf{R}'')^{-1} F_{s''s}^\beta(\mathbf{R}'' - \mathbf{R}) \quad (2.47)$$

This is the result already obtained in previous works [9][10] [11] where expansion up to second order was considered.

Finally we find $\tilde{L}_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'')$.

Third order terms in σ of \tilde{E} can be found from eq.(2.26) substituting $\mathbf{U}^{(1)}$ in third order terms and $\mathbf{U}^{(2)}$ in quadratic terms. So the explicit knowledge of $\left. \frac{\partial^2 U_{\mathbf{R}_s}^\alpha}{\partial \sigma_{\mathbf{R}'s'} \partial \sigma_{\mathbf{R}''s''}} \right|_0$ seems apparently to be needed. But this is not really the case. In fact, collecting all third order terms in which $\left. \frac{\partial^2 U_{\mathbf{R}_s}^\alpha}{\partial \sigma_{\mathbf{R}'s'} \partial \sigma_{\mathbf{R}''s''}} \right|_0$ appears, we obtain:

$$\sum_{\mathbf{T}} \sum_{d\alpha} \left. \frac{\partial^2 U_{\mathbf{T}_s}^\alpha}{\partial \sigma_{\mathbf{R}_s} \partial \sigma_{\mathbf{R}'s'}} \right|_0 \left[\sum_{\mathbf{T}'} \sum_{d'\alpha'} C_{dd'}^{\alpha\alpha'}(\mathbf{T} - \mathbf{T}') \left. \frac{\partial U_{\mathbf{T}'d'}^{\alpha'}}{\partial \sigma_{\mathbf{R}''s''}} \right|_0 - \sum_{s''} F_{ds''}^\alpha(\mathbf{T} - \mathbf{R}'') \right] \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} \quad (2.48)$$

But from eq.(2.40) we see that the expression in brackets vanishes.

This is not accidental; indeed it is a consequence of 2n+1 theorem: with $\mathbf{U}^{(1)}$ it is possible to determine up to the third derivative of $\tilde{E}\{\sigma\}$, which is determined from $E\{U, \sigma\}$ as differential with respect to U . In fact, as already mentioned, (2n+1) theorem is a general property that link the derivatives of a functional that satisfy a variational principle with the derivatives of its internal degrees of freedom.

In conclusion the only terms which give a nonvanishing contribution to the third order in σ are:

$$\begin{aligned}
& \frac{1}{3!} \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \sum_{ss's''} \tilde{L}_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'_{s'}} \sigma_{\mathbf{R}''_{s''}} = \\
& \frac{1}{3!} \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \sum_{ss's''} L_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'_{s'}} \sigma_{\mathbf{R}''_{s''}} \\
& + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \sum_{ss's''} \sum_{\mathbf{T}} \sum_{d\alpha} J_{\alpha}^{(1)}(\mathbf{T} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}_s}} \right|_0 \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'_{s'}} \sigma_{\mathbf{R}''_{s''}} \\
& + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \sum_{ss's''} \sum_{\mathbf{T}\mathbf{T}'} \sum_{d\alpha} \sum_{d'\alpha'} F_{\alpha\alpha'}^{(1)}(\mathbf{T} - \mathbf{R}'', \mathbf{T}' - \mathbf{R}'') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}_s}} \right|_0 \left. \frac{\partial U_{\mathbf{T}'_{d'}}^{\alpha'}}{\partial \sigma_{\mathbf{R}'_{s'}}} \right|_0 \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'_{s'}} \sigma_{\mathbf{R}''_{s''}} \\
& \frac{1}{3!} \sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \sum_{ss's''} \sum_{\mathbf{T}\mathbf{T}'\mathbf{T}''} \sum_{dd'd''} \Phi_{\alpha\alpha'\alpha''}^{(1)}(\mathbf{T} - \mathbf{T}'', \mathbf{T}' - \mathbf{T}'') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}_s}} \right|_0 \left. \frac{\partial U_{\mathbf{T}'_{d'}}^{\alpha'}}{\partial \sigma_{\mathbf{R}'_{s'}}} \right|_0 \left. \frac{\partial U_{\mathbf{T}''_{d''}}^{\alpha''}}{\partial \sigma_{\mathbf{R}''_{s''}}} \right|_0 \sigma_{\mathbf{R}_s} \sigma_{\mathbf{R}'_{s'}} \sigma_{\mathbf{R}''_{s''}}
\end{aligned} \tag{2.49}$$

Symmetrizing:

$$\begin{aligned}
& \tilde{L}_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') = L_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \\
& + \sum_{\mathbf{T}\mathbf{T}'\mathbf{T}''} \sum_{dd'd''} \sum_{\alpha\alpha'\alpha''} \Phi_{\alpha\alpha'\alpha''}^{(1)}(\mathbf{T} - \mathbf{T}'', \mathbf{T}' - \mathbf{T}'') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}_s}} \right|_0 \left. \frac{\partial U_{\mathbf{T}'_{d'}}^{\alpha'}}{\partial \sigma_{\mathbf{R}'_{s'}}} \right|_0 \left. \frac{\partial U_{\mathbf{T}''_{d''}}^{\alpha''}}{\partial \sigma_{\mathbf{R}''_{s''}}} \right|_0 + \\
& + \sum_{\mathbf{T}} \sum_{d\alpha} \left\{ J_{\alpha}^{(1)}(\mathbf{T} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}_s}} \right|_0 + J_{\alpha}^{(1)}(\mathbf{T} - \mathbf{R}, \mathbf{R}'' - \mathbf{R}) \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}'_{s'}}} \right|_0 + \right. \\
& \left. + J_{\alpha}^{(1)}(\mathbf{T} - \mathbf{R}', \mathbf{R} - \mathbf{R}') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}''_{s''}}} \right|_0 \right\} \\
& + \sum_{\mathbf{T}\mathbf{T}'} \sum_{d\alpha} \sum_{d'\alpha'} \left\{ F_{\alpha\alpha'}^{(1)}(\mathbf{T} - \mathbf{R}, \mathbf{T}' - \mathbf{R}) \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}'_{s'}}} \right|_0 \left. \frac{\partial U_{\mathbf{T}'_{d'}}^{\alpha'}}{\partial \sigma_{\mathbf{R}''_{s''}}} \right|_0 + F_{\alpha\alpha'}^{(1)}(\mathbf{T} - \mathbf{R}', \mathbf{T}' - \mathbf{R}') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}''_{s''}}} \right|_0 \left. \frac{\partial U_{\mathbf{T}'_{d'}}^{\alpha'}}{\partial \sigma_{\mathbf{R}_s}} \right|_0 \right. \\
& \left. + F_{\alpha\alpha'}^{(1)}(\mathbf{T} - \mathbf{R}'', \mathbf{T}' - \mathbf{R}'') \left. \frac{\partial U_{\mathbf{T}_d}^{\alpha}}{\partial \sigma_{\mathbf{R}_s}} \right|_0 \left. \frac{\partial U_{\mathbf{T}'_{d'}}^{\alpha'}}{\partial \sigma_{\mathbf{R}'_{s'}}} \right|_0 \right\}
\end{aligned} \tag{2.50}$$

2.2.2 Reciprocal space formulation

First of all let's write in reciprocal space the equation for the r $\{\mathbf{U}, \sigma\}$ -dependent energy per cell:

$$\begin{aligned}
E\{\mathbf{U}, \sigma\}/N &= \epsilon\{\mathbf{U}, \sigma\} = \epsilon_0 + \sum_s K_s \sigma_s(\mathbf{q} = \mathbf{0}) + \\
&\sum_{\mathbf{q}} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s'\alpha'} U_s^\alpha(\mathbf{q})^* C_{ss'}^{\alpha\alpha'}(\mathbf{q}) U_{s'}^{\alpha'}(\mathbf{q}) - \sum_{s\alpha} \sum_{s'} U_s^\alpha(\mathbf{q})^* F_{ss'}^\alpha(\mathbf{q}) \sigma_{s'}(\mathbf{q}) + \frac{1}{2} \sum_s \sum_{s'} \sigma_s(\mathbf{q})^* J_{ss'}(\mathbf{q}) \sigma_{s'}(\mathbf{q}) \right] \\
&+ \sum_{\mathbf{q}\mathbf{q}'} \left[\frac{1}{3!} \sum_{s\alpha} \sum_{s'\alpha'} \sum_{s''\alpha''} \Phi_{1s's''}^{(1)}(\mathbf{q}, \mathbf{q}') U_s^\alpha(\mathbf{q})^* U_{s'}^{\alpha'}(\mathbf{q}') U_{s''}^{\alpha''}(\mathbf{q} - \mathbf{q}') \right] \\
&+ \sum_{\mathbf{q}\mathbf{q}'} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s'\alpha'} \sum_{s''} F_{1s's''}^{(1)}(\mathbf{q}, \mathbf{q}') U_s^\alpha(\mathbf{q})^* U_{s'}^{\alpha'}(\mathbf{q}') \sigma_{s''}(\mathbf{q} - \mathbf{q}') \right] \\
&+ \sum_{\mathbf{q}\mathbf{q}'} \left[\frac{1}{2} \sum_{s\alpha} \sum_{s's''} J_{\alpha}^{(1)}(\mathbf{q}, \mathbf{q}') U_s^\alpha(\mathbf{q})^* \sigma_{s'}(\mathbf{q}') \sigma_{s''}(\mathbf{q} - \mathbf{q}') \right] \\
&+ \sum_{\mathbf{q}\mathbf{q}'} \left[\frac{1}{3!} \sum_{ss's''} L_{1ss's''}(\mathbf{q}, \mathbf{q}') \sigma_s(\mathbf{q})^* \sigma_{s'}(\mathbf{q}') \sigma_{s''}(\mathbf{q} - \mathbf{q}') \right]
\end{aligned}$$

where ϵ is the energy per cell, and where we have defined:

$$O(\mathbf{q}) = \sum_{\mathbf{R}} O(\mathbf{R} - \mathbf{R}') e^{-i\mathbf{q}(\mathbf{R}-\mathbf{R}')} \quad , \quad O(\mathbf{R} - \mathbf{R}') = \frac{1}{N} \sum_{\mathbf{q}} O(\mathbf{q}) e^{i\mathbf{q}(\mathbf{R}-\mathbf{R}')} \quad (2.51)$$

and

$$P(\mathbf{q}, \mathbf{q}') = \sum_{\mathbf{R}\mathbf{R}'} P(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') e^{-i\mathbf{q}(\mathbf{R}-\mathbf{R}'')} e^{i\mathbf{q}'(\mathbf{R}'-\mathbf{R}'')}$$

from which:

$$P(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') = \frac{1}{N^2} \sum_{\mathbf{q}} P(\mathbf{q}, \mathbf{q}') e^{i\mathbf{q}(\mathbf{R}-\mathbf{R}'')} e^{-i\mathbf{q}'(\mathbf{R}'-\mathbf{R}'')}$$

where N is the number of cells over which the periodic boundary conditions are to be taken; We briefly recall some properties of the transformed entities which appear in the expansion.

First of all, all the Fourier transformed of real quantities have the following property:

$$O(\mathbf{q})^* = O(-\mathbf{q}) \quad (2.52)$$

So, for example, $U_s^\alpha(\mathbf{q})^* = U_s^\alpha(-\mathbf{q})$, besides $C_{ss'}^{\alpha\alpha'}(\mathbf{q})^* = C_{ss'}^{\alpha\alpha'}(-\mathbf{q})$ etc.

Furthermore, the quantities $C_{ss'}^{\alpha\alpha'}(\mathbf{q})$ and $J_{ss'}(\mathbf{q})$ have another important property due to the symmetry for index exchange:

$$C_{ss'}^{\alpha\alpha'}(\mathbf{q}) = C_{s's}^{\alpha'\alpha}(-\mathbf{q}) \quad (2.53)$$

$$J_{ss'}(\mathbf{q}) = J_{s's}(-\mathbf{q})$$

For what concerns the 3^d order coefficients in reciprocal space, they have the following properties due to the reality of the transformed entities:

$$O(\mathbf{q}, \mathbf{q}')^* = O(-\mathbf{q}, -\mathbf{q}')$$

which is analog to eq.(2.52).

The properties for index exchange are more complex than the analogous eq. (2.53).

The following relationships are thus obtained:

$$\begin{aligned}\Phi_{\alpha\alpha'\alpha''}^{(1)}(q, q') &= \Phi_{\alpha'\alpha\alpha''}^{(1)}(-q', -q) = \Phi_{\alpha\alpha''\alpha'}^{(1)}(q, q - q') = \Phi_{\alpha''\alpha'\alpha}^{(1)}(q' - q, q') \\ F_{\alpha\alpha'}^{(1)}(q, q') &= F_{\alpha'\alpha}^{(1)}(-q', -q) \\ J_{\alpha}^{(1)}(q, q') &= J_{\alpha}^{(1)}(q, q - q') \\ L_{ss's''}(q, q') &= L_{s'ss''}(-q', -q) = L_{ss''s'}(q, q - q') = L_{s''s's}(q' - q, q')\end{aligned}$$

Keeping this in mind, we can write (2.35) in reciprocal space:

$$\begin{aligned}\tilde{\epsilon}\{\sigma\} &= \epsilon_o + \sum_s K_s \sigma_s(q=0) + \frac{1}{2} \sum_q \sum_s \sum_{s'} \sigma_s(q)^* \tilde{J}_{ss'}(q) \sigma_{s'}(q) \\ &\quad + \sum_{qq'} \left[\frac{1}{3!} \sum_{ss's''} \tilde{L}_{ss's''}(q, q') \sigma_s(q)^* \sigma_{s'}(q') \sigma_{s''}(q - q') \right]\end{aligned}$$

Now we want to see how (2.47) and (2.50) are transformed in reciprocal space. For what concerns (2.47), we just need to multiply by $e^{-iq(\mathbf{R}-\mathbf{R}')}$ and sum over \mathbf{R} . We then obtain:

$$\tilde{J}_{ss'}(q) = J_{ss'}(q) - \sum_{d\alpha} \sum_{s''\beta} F_{s''s}^{\beta}(q)^* C_{s''d}^{\beta\alpha}(q)^{-1} F_{ds'}^{\alpha}(q) \quad (2.54)$$

where (2.52) and (2.53) have been used.

Before transforming (2.50), let's write (2.40) in a more proper way:

$$\begin{aligned}\left. \frac{\partial U_{\bar{\mathbf{R}}_s}^{\bar{\alpha}}}{\partial \sigma_{\mathbf{R}'s'}} \right|_0 &= \sum_{\mathbf{R}} \sum_{s\alpha} \left(\frac{1}{N} \sum_q C_{\bar{s}s}^{\bar{\alpha}\alpha}(q)^{-1} e^{iq(\bar{\mathbf{R}}-\mathbf{R})} \right) F_{ss'}^{\alpha}(\mathbf{R}-\mathbf{R}') \\ &= \frac{1}{N} \sum_q \sum_{s\alpha} C_{\bar{s}s}^{\bar{\alpha}\alpha}(q)^{-1} e^{iq(\bar{\mathbf{R}}-\mathbf{R}')} \left(\sum_{\mathbf{R}} F_{ss'}^{\alpha}(\mathbf{R}-\mathbf{R}') e^{-iq(\mathbf{R}-\mathbf{R}')} \right) \\ &= \frac{1}{N} \sum_q \left(\sum_{s\alpha} C_{\bar{s}s}^{\bar{\alpha}\alpha}(q)^{-1} F_{ss'}^{\alpha}(q) \right) e^{iq(\bar{\mathbf{R}}-\mathbf{R}')} \\ &= \frac{1}{N} \sum_q D_{\bar{s}s'}^{\bar{\alpha}}(q) e^{iq(\bar{\mathbf{R}}-\mathbf{R}')} \end{aligned}$$

Now multiplying (2.50) by $e^{-iq(\mathbf{R}-\mathbf{R}'')} e^{iq'(\mathbf{R}'-\mathbf{R}'')}$ and summing over \mathbf{R}, \mathbf{R}' we obtain:

$$\begin{aligned}
\tilde{L}_{ss's''}(\mathbf{q}, \mathbf{q}') = & \\
& L_{ss's''}(\mathbf{q}, \mathbf{q}') + \sum_{dd'd''} \sum_{\alpha\alpha'\alpha''} \Phi_{\alpha\alpha'\alpha''}^{(1)}(\mathbf{q}, \mathbf{q}') D_{ds}^{\alpha}(-\mathbf{q}) D_{d's'}^{\alpha'}(\mathbf{q}') D_{d''s''}^{\alpha''}(\mathbf{q} - \mathbf{q}') + \\
& + \sum_{d\alpha} \left\{ J_{ds's''}^{(1)}(\mathbf{q}, \mathbf{q}') D_{ds}^{\alpha}(-\mathbf{q}) + J_{ds''s}^{(1)}(-\mathbf{q}', \mathbf{q} - \mathbf{q}') D_{ds'}^{\alpha}(\mathbf{q}') + J_{d'ss'}^{(1)}(\mathbf{q}' - \mathbf{q}, -\mathbf{q}) D_{ds''}^{\alpha}(\mathbf{q} - \mathbf{q}') \right\} + \\
& + \sum_{d\alpha} \sum_{d'\alpha'} \left\{ F_{dd's}^{(1)}(-\mathbf{q}', \mathbf{q} - \mathbf{q}') D_{ds'}^{\alpha}(\mathbf{q}') D_{d's''}^{\alpha'}(\mathbf{q} - \mathbf{q}') + F_{dd's'}^{(1)}(\mathbf{q}' - \mathbf{q}, -\mathbf{q}) D_{ds''}^{\alpha}(\mathbf{q} - \mathbf{q}') D_{d's}^{\alpha'}(-\mathbf{q}) + \right. \\
& \left. + F_{dd's''}^{(1)}(\mathbf{q}, \mathbf{q}') D_{ds}^{\alpha}(-\mathbf{q}) D_{d's'}^{\alpha'}(\mathbf{q}') \right\}
\end{aligned}$$

2.3 Formation energy

It is more practical and accurate to deal with microscopic and macroscopic relaxation effects separately, treating the elastic (macroscopic) term exactly and using eq.(2.26) for the microscopic relaxation only. To this end, we define the alloy formation energy, $\Delta E(\{\sigma_{\mathbf{R}_s}\}, \Omega)$, as the difference between the energy of the alloy in a given configuration $\{\sigma_{\mathbf{R}_s}\}$ and at a given molar volume Ω , and the appropriate average of those of the pure components at their respective equilibrium volumes:

$$\Delta E(\{\sigma_{\mathbf{R}_s}\}, \Omega) = E(\{\sigma_{\mathbf{R}_s}\}, \Omega) - x E_A(\Omega_A) - (1-x) E_B(\Omega_B) \quad (2.55)$$

where $E_{A,B}$ and $\Omega_{A,B}$ are the equilibrium energies and volumes of the pure materials, and $x = \frac{\langle \sigma_{\mathbf{R}_s} \rangle + 1}{2}$ is the molar composition of the $A_x B_{1-x}$ alloy. The formation energy can now be split into an elastic contribution, ΔE_{elast} , plus a configurational contribution, ΔE_{config} , where:

$$\Delta E_{elast}(x, \Omega) = x(E_A(\Omega) - E_A(\Omega_A)) + (1-x)(E_B(\Omega) - E_B(\Omega_B)) \quad (2.56)$$

is the energy paid to bring the two pure materials from their equilibrium volumes to the volume of the alloy and does not depend on the microscopic configuration but only on the macroscopic concentration x , and

$$\Delta E_{config}(\{\sigma_{\mathbf{R}s}\}, \Omega) = E(\{\sigma_{\mathbf{R}s}\}, \Omega) - xE_A(\Omega) - (1-x)E_B(\Omega) \quad (2.57)$$

is the formation energy of the alloy at the fixed volume Ω . The elastic energy ΔE_{elast} can be easily calculated from the equations of state for the pure components, whereas the configurational energy ΔE_{config} is computed from the perturbative expansion of eq.(2.35) using the \tilde{K}_s 's, the $\tilde{J}_{ss'}$'s and $\tilde{L}_{ss's''}$'s appropriate to the volume Ω . Thus we have:

$$\begin{aligned} \Delta E_{config}^{(1)}(\{\sigma_{\mathbf{R}s}\}, \Omega) &= \sum_{\mathbf{R}s} \tilde{K}_s \sigma_{\mathbf{R}s} - (2x-1)N \sum_s \tilde{K}_s \\ &= \sum_s \tilde{K}_s \left(\sum_{\mathbf{R}} \sigma_{\mathbf{R}s} \right) - (2x-1)N \sum_s \tilde{K}_s \\ &= N \sum_s (2x_s - 1) \tilde{K}_s - N(2x-1) \sum_s \tilde{K}_s \end{aligned}$$

where N is the number of cells, and

$$\sum_{\mathbf{R}} \sigma_{\mathbf{R}s} = (2x_s - 1)N \quad , \quad \sum_s x_s = x n_{\text{spc}} \quad , \quad \sum_{\mathbf{R}s} \sigma_{\mathbf{R}s} = (2x-1)N n_{\text{spc}} \quad (2.58)$$

where n_{spc} is the number of sites per primitive cell ($n_{\text{spc}} = \sum_s 1$) and x_s is a concentration per sublattice (indexed by s) with s running over all substitutional sites per cell. Note

that if $n_{\text{SPC}} = 1$, as in our particular system, it is easy to see that $\Delta E_{\text{config}}^{(1)}(\{\sigma_{\mathbf{R}s}\}, \Omega) = 0$.

Further terms in ΔE_{config} are:

$$\Delta E_{\text{config}}^{(2)}(\{\sigma_{\mathbf{R}s}\}, \Omega) = \frac{1}{2} \left(\sum_{\mathbf{R}\mathbf{R}'} \sum_{ss'} \tilde{j}_{ss'}^{(\Omega)}(\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}s} \sigma_{\mathbf{R}'s'} - N \sum_{\mathbf{R}} \sum_{ss'} \tilde{j}_{ss'}^{(\Omega)}(\mathbf{R}) \right) \quad (2.59)$$

$$\begin{aligned} & \Delta E_{\text{config}}^{(3)}(\{\sigma_{\mathbf{R}s}\}, \Omega) = \\ & \frac{1}{3!} \left(\sum_{\mathbf{R}\mathbf{R}'\mathbf{R}''} \sum_{ss's''} \tilde{L}_{ss's''}^{(\Omega)}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') \sigma_{\mathbf{R}s} \sigma_{\mathbf{R}'s'} \sigma_{\mathbf{R}''s''} - (2x - 1) N \sum_{\mathbf{R}\mathbf{R}'} \sum_{ss's''} \tilde{L}_{ss's''}^{(\Omega)}(\mathbf{R}, \mathbf{R}') \right) \end{aligned} \quad (2.60)$$

3 Energetics

In the preceding chapter we have seen the techniques and the method used to calculate the energy of a crystal (DFT) and its derivatives (DFPT). Now we want to check the accuracy of that method in describing the energetics of our specific system, verifying up to which perturbative order of the alloy expansion of eq.(2.35) are to be kept to obtain the precision required for our computational purposes. Before proceeding we want to specify once for all some general technical aspects with which all our present calculations have been performed. In our present calculations we have used the LDA approximation of the exchange and correlation term of the electron gas, as obtained by Ceperley and Alder [22], using Perdew and Zunger [23] parametrization.

In the spirit of following and further developing the work done in [10], we used the same $v_s^{loc}(r)$ and the same $v_{s,l}(r)$, generated according to the prescription of Von Barth and Car [40] but in the Kleinman and Bylander (KB) form. The comparison of the results up to 2^{nd} order with the results obtained in ref [10] is also a check of reliability of the pseudopotentials.

All self-consistent calculations have been performed with plane waves up to a kinetic-

energy cutoff of 16 Ryd, while Brillouin zone integrations have been performed using 10 special Monkhorst and Pack [24] k-points in the case of zincblende and with equivalent points refolded in the Brillouin zone for all other considered supercells. In this way the computational convergence is obtained with a better precision as systematic errors, due to the possibly incomplete Brillouin zone sampling, cancel out to a large extent.

3.1 GaInP system

The alloy considered in the present study is in particular the pseudobinary alloy $\text{Ga}_x\text{In}_{1-x}\text{P}$, which is a prototype of $\text{A}_x\text{B}_{1-x}\text{C}$ alloys, with A and B of group III and C of group V. Its structure is based on a zincblende type lattice, which means that it's made up of 2 FCC sublattices shifted of $a_0(1/4,1/4,1/4)$; one of them is occupied by the P anions, while the sites of the other one are occupied randomly by the cations Ga and In with a probability proportional to the respective concentrations. So $\text{Ga}_x\text{In}_{1-x}\text{P}$ is a substitutional pseudobinary alloy of cationic type.

Lattice parameter, bulk modulus and its derivative with respect to pressure are the first structural quantities of interest for a first principles calculation applied to solids. It has been recognized [36] that the correct way to determine these parameters is to fit the total energy calculations with some universal equation of state for solids (in our case with Murnaghan equation [37]) which depends on these few parameters. The results of the fit obtained with 10 k-points is shown in table 3.1:

| | a_o (a.u.) | B (kbar) | B' |
|----------|--------------|----------|------|
| GaP | | | |
| th. | 10.212 | 889 | 4.45 |
| exp.[38] | 10.301 | 914 | 4.79 |
| InP | | | |
| th. | 10.982 | 714 | 4.50 |
| exp.[38] | 11.090 | 725 | 4.59 |

Table 3.1: Comparison between theoretical and experimental structural properties of GaP and InP

3.2 Ordered structures

Now we have all the instruments to study the structural and energetical properties of arbitrary configurations of atoms in a lattice. First of all, 2^{nd} order terms J , F and C are obtained for a (444) mesh in \mathbf{q} space and the respective $\tilde{J}(\mathbf{q})$ are computed for a (888) mesh, using interpolation for the lacking values. But \tilde{J} has a longer range than J , F and C , so we prefer to interpolate J , F and C , which are well converged and smooth in \mathbf{q} space, and then compute the respective $\tilde{J}(\mathbf{q})$ for the larger mesh. Their Fourier Transform gives finally the $\tilde{J}(\mathbf{R})$ for a FCC cell made up of 512 elemental cells, each with an alloy atom (cation) and a phosphorus (this will be the supercell for the Monte Carlo simulation).

The whole procedure just described cannot be done for any cell volume. That's why the renormalized force constants $\tilde{J}_{(\Omega)}(\mathbf{R})$ are computed at 3 different lattice parameters ($a_o=10.236, 10.683, 10.971$ a.u.) and interpolated quadratically for all intermediate values.

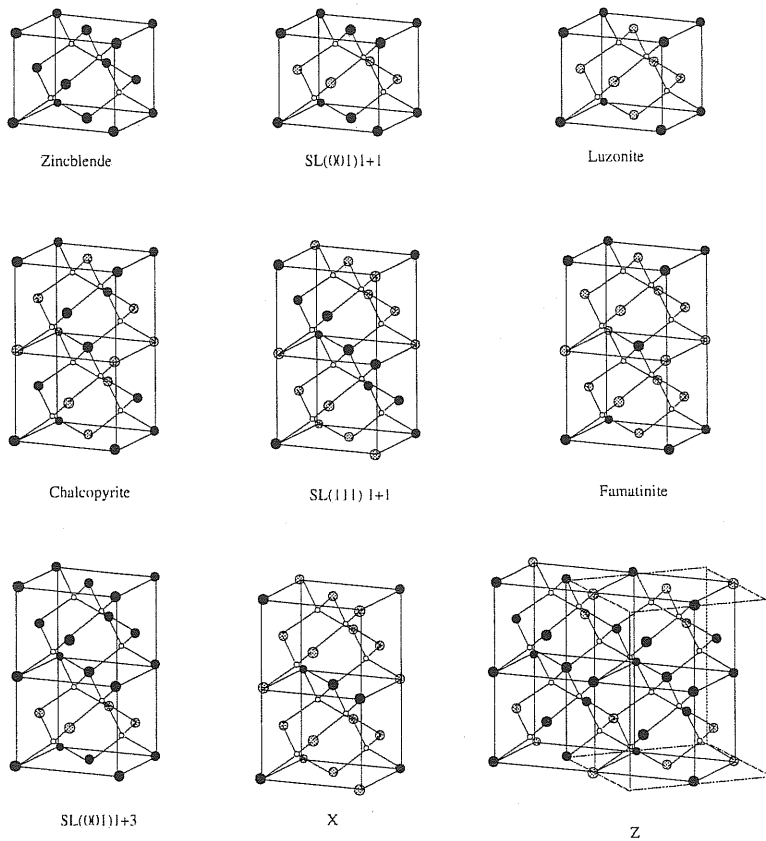


Figure 3.1:

To test the accuracy of second order DFPT, we compare the energy results obtained with our method against non-perturbative calculations for some relatively small ordered structures in the unrelaxed and relaxed case. The selected supercells are shown in fig.3.1

Results are shown in tab 3.2

From table 3.2 we see that most of the configuration energy comes from relaxation contributions. Structures such as Chalcopyrite, $SL(001)_{1+1}$ and $SL(111)_{1+1}$ with inversion symmetry with respect to σ sign (which means that $\{-\sigma\}$ gives the same structure as $\{\sigma\}$, implying the condition $x = 0.5$) do not have any third order contribution in the ΔE_{config} ,

and we can see that the relative error in the relaxed case is at most around 3.5% (2% of mean error) which is usually of 1 meV/atom. On the contrary, for all other structures, in which third order terms are present, the relative error can be also of 10-14% (3-4 meV/atom). We then decide to go further in the energy expansion.

| Structure | | fixed atoms | | relaxed atoms | |
|------------------------|---|-------------|-------|---------------|--------|
| | | SCF | LRT | SCF | LRT |
| SL[001] ₁₊₁ | <i>GaInP</i> ₂ | -1.46 | -1.52 | -40.18 | -41.70 |
| SL[111] ₁₊₁ | <i>GaInP</i> ₂ | -1.05 | -1.02 | -29.93 | -30.26 |
| Calcopryrite | <i>Ga</i> ₂ <i>In</i> ₂ <i>P</i> ₄ | -1.66 | -1.69 | -52.45 | -53.52 |
| Luzonite | <i>Ga</i> ₁ <i>In</i> ₃ <i>P</i> ₄ | -1.09 | -1.14 | -33.01 | -31.28 |
| Luzonite | <i>Ga</i> ₃ <i>In</i> ₁ <i>P</i> ₄ | -1.10 | -1.14 | -27.56 | -31.28 |
| Famatinite | <i>Ga</i> ₁ <i>In</i> ₃ <i>P</i> ₄ | -1.18 | -1.22 | -39.27 | -37.18 |
| Famatinite | <i>Ga</i> ₃ <i>In</i> ₁ <i>P</i> ₄ | -1.19 | -1.22 | -33.47 | -37.18 |
| X | <i>Ga</i> ₂ <i>In</i> ₆ <i>P</i> ₈ | -0.88 | -0.89 | -26.42 | -25.55 |
| X | <i>Ga</i> ₆ <i>In</i> ₂ <i>P</i> ₈ | -0.89 | -0.89 | -23.76 | -25.55 |
| SL[001] ₁₊₃ | <i>Ga</i> ₁ <i>In</i> ₃ <i>P</i> ₄ | -0.69 | -0.70 | -30.67 | -31.05 |
| SL[001] ₁₊₃ | <i>Ga</i> ₃ <i>In</i> ₁ <i>P</i> ₄ | -0.69 | -0.70 | -29.37 | -31.05 |
| Z | <i>Ga</i> ₅ <i>In</i> ₁₁ <i>P</i> ₁₆ | -1.07 | -1.07 | -38.94 | -38.02 |
| Z | <i>Ga</i> ₁₁ <i>In</i> ₅ <i>P</i> ₁₆ | -1.07 | -1.07 | -35.40 | -38.02 |

Table 3.2: ΔE_{config} ($a_o = 10.683a.u.$) (energy in meV/atom)

3.3 Third order

In the preceding chapter we have seen that, in principle, all the instruments to compute the third order renormalized force constants \tilde{L} are available with just the linear response $\Delta n(\mathbf{r})$ to substitutional (σ) and displacive (U) perturbations.

Nevertheless, from second order results we expect the 3^{rd} order contributions to be small (of the order of some meV's for relaxed structures); besides the computational effort appears to be much bigger than the one required for the 2^{nd} order terms. That's why we try to proceed in another way. In fact we fit these 3^{rd} order terms in such a way to reproduce their total energy contributions to the previously shown structures (luzonite, famatinitite etc.). Our basic hypothesis is that only few terms $\tilde{L}_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'')$ are important. As a first rude assumption we suppose that $\tilde{L}_{ss's''}(\mathbf{R} - \mathbf{R}'', \mathbf{R}' - \mathbf{R}'') = 0$ unless at least 2 cationic pairs are nearest neighbours. This choice is guided by two considerations:

- the strongest 2 body interactions are those between nearest neighbours;
- we presume that the change of these interactions is a decreasing function of the distance of a third atom perturbation.

Exploiting the symmetry of zincblende structure, it can be shown that only 5 different 3-body interaction terms may satisfy our constraints and then possibly be different from zero (fig. 3.2).

We found that only fig. a, b and e are important in the description of the third order term in eq. (2.60), corresponding to figures that contain only first neighbours in the cationic sublattice (a and b) or atoms that are aligned along chains of bonds in $[110]$ planes. As

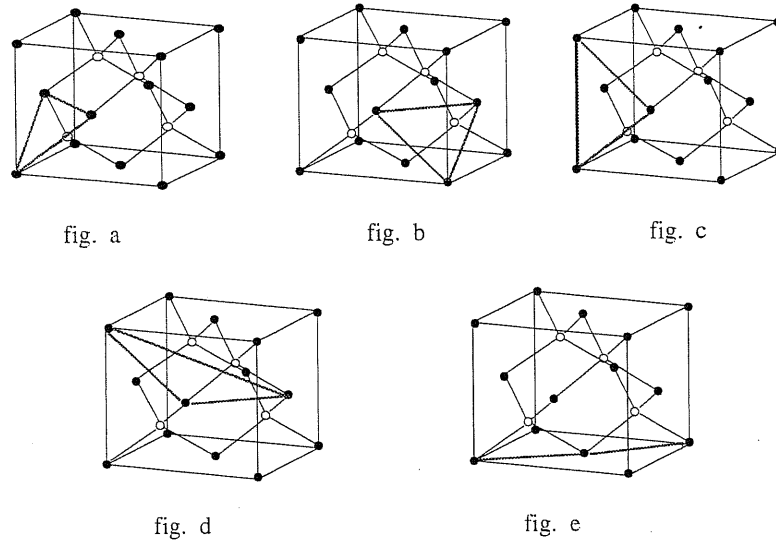


Figure 3.2:

figures a and b enter with different weights only in the description of structure Z (this is the reason why we added it to the other, more standard [39] structures) we considered two kind of fit: i) one where fig. a and b were given the same weight and ii) one where fig. a was (arbitrarily) taken to vanish. The resulting best-fit values for the two fits are:

$$1) \text{fig.a}=\text{fig.b}=-0.335 \text{ meV}, \quad \text{fig.e}=-0.125 \text{ meV}$$

$$2) \text{fig.a}=0, \quad \text{fig.b}=-0.67 \text{ meV}, \quad \text{fig.e}=-0.125 \text{ meV}$$

Results are shown in table 3.3 for mixed structures. The mean error is decreased from 3-4 meV/atom to 1 meV/atom (10-14% to 2-4%) which is similar to the error present in the symmetric structures where third order terms are not present.

On the basis of these results we cannot discriminate on the relative importance of fig.a and b and in the following the results of both parametrizations will be considered.

Now we have all the quantities we need to compute the energy of whatever supercell

| Structure | | relaxed atoms | | | |
|------------------------|---------------------|---------------|--------|-------------------------|-------------------------|
| | | SCF | LRT | LRT+3 rd (1) | LRT+3 rd (2) |
| Luzonite | $Ga_1In_3P_4$ | -33.01 | -31.28 | -33.94 | -33.94 |
| Luzonite | $Ga_3In_1P_4$ | -27.56 | -31.28 | -28.62 | -28.62 |
| Famatinite | $Ga_1In_3P_4$ | -39.27 | -37.18 | -40.35 | -40.35 |
| Famatinite | $Ga_3In_1P_4$ | -33.47 | -37.18 | -34.02 | -34.02 |
| X | $Ga_2In_6P_8$ | -26.42 | -25.55 | -26.88 | -26.88 |
| X | $Ga_6In_2P_8$ | -23.76 | -25.55 | -24.22 | -24.22 |
| SL[001] ₁₊₃ | $Ga_1In_3P_4$ | -30.67 | -31.05 | -31.55 | -31.55 |
| SL[001] ₁₊₃ | $Ga_3In_1P_4$ | -29.37 | -31.05 | -30.54 | -30.54 |
| Z | $Ga_5In_{11}P_{16}$ | -38.94 | -38.02 | -39.43 | -39.70 |
| Z | $Ga_{11}In_5P_{16}$ | -35.40 | -38.02 | -36.60 | -36.44 |

Table 3.3: ΔE_{config} ($a_o = 10.683a.u.$) (energy in meV/atom)

with 2-4% of error. The next step is to determine the thermodynamics of the system.

4 Thermodynamics

In the preceding chapter we have verified that, with the method explained in chapter 2, we are able to compute from first principles the energy of any configuration in a rapid way and with an error of 1-2% with respect to DFT results. We can now face the problem of determining the solid solutions phase diagram of $Ga_xIn_{1-x}P$ and the analysis of their thermodynamical properties at finite temperature. At temperature different from zero the entropic effects become of fundamental importance in governing the relative stability of the various possible phases. For the solution of the thermodynamical problem we use the principles and techniques of statistical mechanics. Nevertheless, three remarks are to be done:

- we will limit ourself to examine only configurations reachable by expansion of the virtual crystal around the zincblende equilibrium structure (which is the equilibrium structure of the pure compounds)
- at the considered temperatures, the electrons can be considered in a good approximation in their ground state, so that the Born-Oppenehimer approximation is still valid
- we neglect the thermal expansion of the alloy.

In conclusion we assume that the only main thermal effects are of entropic (configurational) nature, leaving the energetics unchanged.

Now we will proceed to the theoretical analysis of the thermodynamical system, then to the statistical and computational techniques used to solve it, and finally we will show our results.

4.1 Finite temperature thermodynamics

The most natural conditions in which phase transitions are studied are those of constant pressure, P , and temperature, T . The most appropriate thermodynamical potential for describing such a system is the Gibbs free energy:

$$G = G(P, T, N_{tot}) = E + PV - TS \quad (4.1)$$

For describing a system where many components are present, every one with N_i particles, we introduce the chemical potentials μ_i , conjugated to the N_i variables, defined as:

$$\mu_i = \left(\frac{\partial E}{\partial N_i} \right)_{S, V, N_{j \neq i}} = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}} \quad (4.2)$$

From Euler theorem for homogeneous functions, G reduces to

$$G = \sum_i \mu_i N_i \quad (4.3)$$

For our present system, in which only two variable components are present, only one

concentration is the independent variable (let's say $x = N_1/N$), and G simply reduces to:

$$G = N(\Delta\mu \cdot x + \mu_2) \quad (4.4)$$

so that only one concentration is the independent variable, and its conjugate one is $\Delta\mu = \mu_1 - \mu_2$.

In general, the most stable phase at fixed (P,T) is the phase minimizing G , so that G results a concave function with respect to concentration. The condition of local stability with respect to local fluctuations with fixed numbers of atoms can be written as:

$$\frac{\partial \Delta\mu}{\partial x} \geq 0 \quad (4.5)$$

When this condition is not satisfied, the system tends to segregate. This can be clearly seen examining fig.4.1 where the theoretical Gibbs free energy of the homogeneous system is shown for two different situations at $T=640$ K and $T=1000$ K, both at $P=0$.

For $T=1000$ K the stability condition is always satisfied, and the system will always be homogeneous. For $T=640$ K the system shows a miscibility gap occurring between the two values of the concentration having the same $\Delta\mu$ (pointed by arrows in fig.4.1), that is found by the common tangent construction. From a geometrical point of view, the thermodynamically stable concentrations are all those whose tangent line is a lower bound to the free energy in any other point. The spinodal points (open circles in fig.4.1) are located instead in correspondence of the flex points of F . The region between the edges of the miscibility gap and the spinodal points is metastable: the system is stable with respect to local fluctuations of the composition but unstable with respect to global segregation.

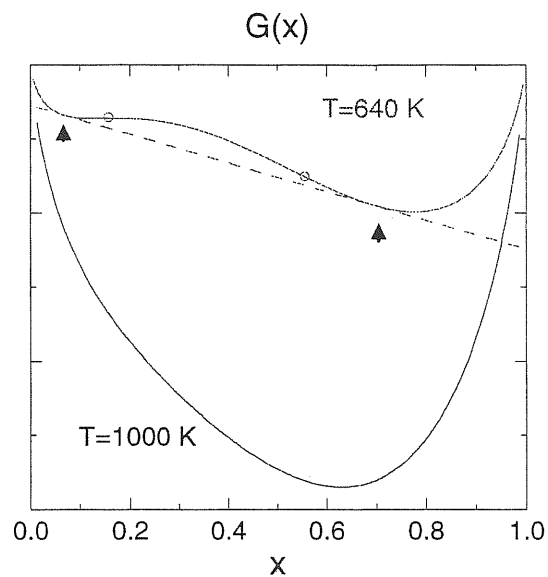


Figure 4.1: Computed Gibbs free energy for $T=640$ K and $T=1000$ K, both at $P=0$

The region between the two spinodal points is, due to the concavity of the free energy, completely unstable.

So in the range of concentrations of the miscibility gap, the physical G follows the tangent line and the system separates in the two extreme concentration phase with relative fraction determined by the usual lever rule. The critical temperature T_c , at which the miscibility gap reduces to zero, is clearly intermediate between the two cases shown in fig. 4.1.

Thus the thermodynamics of our system is completely determined once we know the free energy G . The link between microscopic energetics and thermodynamics is statistics. From a statistical point of view, the thermodynamical properties of any system at fixed

temperature T can be obtained by standard Boltzmann averages:

$$\langle O \rangle = \frac{\sum_C O[C] e^{-\beta E[C]}}{\sum_C e^{-\beta E[C]}} = \frac{\sum_C O[C] e^{-\beta E[C]}}{Z} \quad (4.6)$$

where C denotes a microscopic configuration of the system, $E[C]$ its free energy, $O[C]$ the corresponding value of the relevant observable, β is $(k_b T)^{-1}$, and Z the partition function. This means that the normalized probability of finding the system in microstate C is:

$$P_T[C] = \frac{e^{-\beta E[C]}}{Z} \quad (4.7)$$

The evaluation of this multidimensional integral can be performed by Monte Carlo methods: the interaction constants previously computed are used to carry out lattice-gas Monte Carlo simulations from which we calculate the finite-temperature properties of the system. We should sample the phase space with probability distribution proportional to (4.7) using the standard Metropolis algorithm, so, imposing detailed balance, the transition probability results to be:

$$T_{i,j} = \min \left[e^{-\beta(E[C_j] - E[C_i])}, 1 \right] \quad (4.8)$$

For our statistical ensemble where also the pressure P is fixed the partition function results to be:

$$\tilde{Z}_{N_{tot}, P, T} = \int dV \sum_C e^{-\beta(E[C] + PV)} \equiv e^{-\beta G} \quad (4.9)$$

so the normalized probability is:

$$P_{N_{tot},P,T}[C,V] = \frac{e^{-\beta(E[C]+PV)}}{Z} \quad (4.10)$$

G is then easily obtained using thermodynamic integration: G derivatives are in fact physical observables whose averages can be computed as stated above using important sampling. This can be easily understood considering a reversible transformation between 2 states A and B governed by the external parameter λ , so that:

$$G(B) - G(A) = \int_A^B \frac{\partial G}{\partial \lambda} d\lambda \quad (4.11)$$

In our specific case, using the number of particles N_1 , we have:

$$G(B) - G(A) = \int_A^B \left(\frac{\partial G}{\partial N_1} \right)_{T,P} dN_1 = \int_A^B \langle \Delta\mu(x) \rangle dx \quad (4.12)$$

In this way the knowledge of $\Delta\mu(x)$ for all values of x of a given interval leads to the determination of ΔG for all intermediate states. Finally some problems could arise when we try to evaluate $\Delta\mu(x)$ for x in the region of the miscibility gap. In this case the system could have metastable domains whose surface energy contributions could be important in a finite size supercell. So we prefer another way to get $\Delta\mu(x)$, performing our simulations at fixed $\Delta\mu$. So in practice the function $x(\Delta\mu)$ is determined: simulations are thus developed at constant T, P and $\Delta\mu$, in a "quasi grand canonical" ensemble, in the sense that the total number of particles is fixed (in our case using a supercell of 1024 atoms), but the equilibrium concentration is determined by the value of its conjugate potential. With this procedure any segregating tendency of the alloy comes out with the appearance of hysteresis cycles.

Therefore the simulation steps are performed attempting two different types of Monte Carlo moves: the reversal (flipping) of the spin attached to each particle and a variation of the volume of the supercell. The trial move is accepted with the Metropolis probability:

$$p = \min \left\{ \exp \left[-\beta(\Delta H - \Delta\mu\Delta N_1) \right], 1 \right\}, \quad (4.13)$$

where $\Delta H = \Delta E - P\Delta V$ is the enthalpy variation associated to the move, and ΔN_1 is the variation of the number of particles of type 1. The single-spin-flipping-based algorithm is known in literature as *Glauber dynamics* [43]. For each fixed temperature we perform the simulations starting with very large and positive values of the chemical potential for which GaP is clearly more stable than InP, and then decreasing it slowly towards a In-rich region. For every value of $\Delta\mu$ we perform a large number (1000÷2000) of MonteCarlo trial moves per site, to be sure that thermal equilibrium is actually reached and to lower the statistical error. Each constant $\Delta\mu$ simulation starts with the last configuration of the previous one (with a slightly different chemical potential). Then we sample the configurational space of the system moving in the opposite direction, beginning with a large and negative value of $\Delta\mu$ and increasing it with small steps.

For convenience, the dependence of $\Delta\mu$ upon concentration is fitted by the analytical function:

$$\Delta\mu(x) = k_B T \log \left(\frac{x}{1-x} \right) + \frac{dP(x)}{dx} + \Delta E, \quad (4.14)$$

where the first term is the entropy of a perfectly random solution, $P(x)$ is a fourth- or sixth-order polynomial constrained to vanish for $x = 0, 1$, and ΔE is the energy difference between the pure materials (corresponding to the same limits).

In this way we can estimate the $\Delta\mu(x)$ function in the range of concentrations where the system is unstable and no function points are available. In fig.4.2 the $\Delta\mu(x)$ function for $T=640$ K and $T=1000$ K are shown, the integration of which gives the G functions previously shown in fig.4.1.

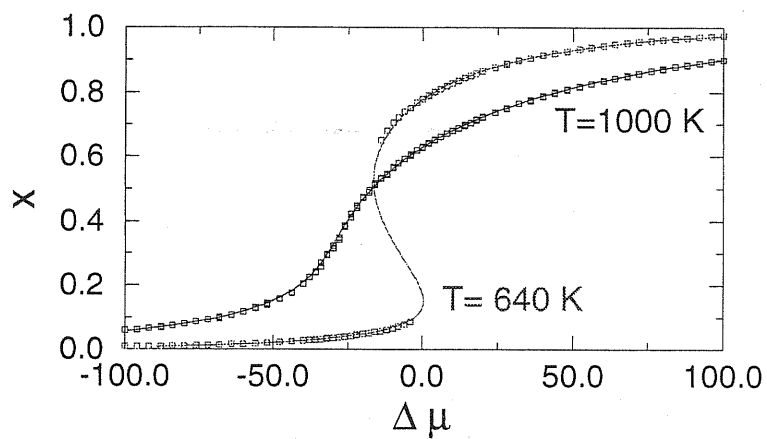


Figure 4.2: $\Delta\mu(x)$ function for $T=640$ K and $T=1000$ K, both at $P=0$; squares mark the computed points, the continuous lines are the fitted functions

4.2 Phase diagrams

Now we just let our machinery work and produce the phase diagram, that is the variation of the miscibility gap with temperature at fixed pressure (our calculations were performed always at $P=0$). Our aim was to verify the influence of third order terms corrections on the final phase diagram, so we produced it both excluding and including third order contributions. First of all in fig.4.3 we compare our results obtained including only second order terms with those already available in ref.[10], in order to check the insensitivity on the pseudopotential form, and so its reliability.

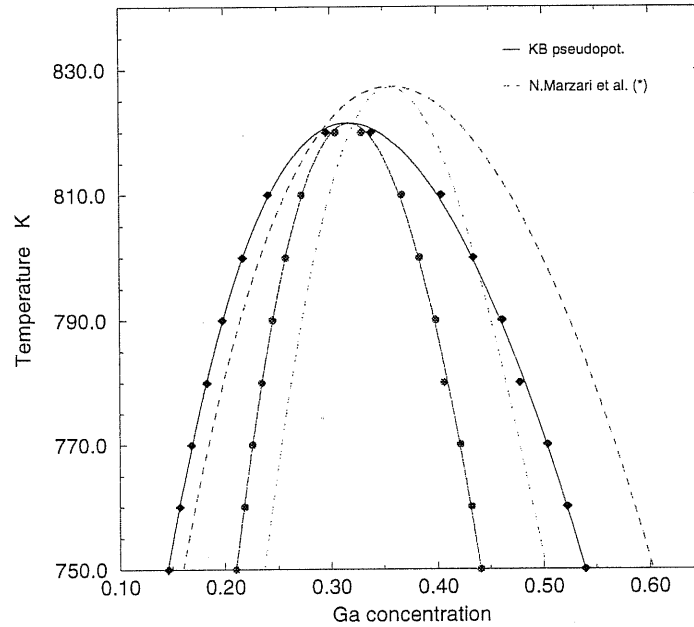


Figure 4.3: Comparison between present calculation and results from ref[10] for phase diagram including up to second order terms but using a different pseudopotential form

Results for T_c and x_c are reported in table 4.1. In our present calculations T_c is slightly

| | ref[10] | 2 nd ord. | 3 rd ord. | exp.[44] |
|-----------|---------|----------------------|----------------------|----------|
| T_c (K) | 830 | 820 | 730 | 930 |
| x_c | 0.35 | 0.32 | 0.34 | 0.6 |

Table 4.1:

lowered (less than 10 K) and also x_c is substantially unchanged. Also the two shapes are very similar indeed. So the pseudopotential form dependence is very weak.

Finally we show the phase diagrams obtained with third order terms inclusion, compared with the phase diagram previously obtained. Both parametrizations of three-body figures give the same phase diagram, shown in fig. 4.4.

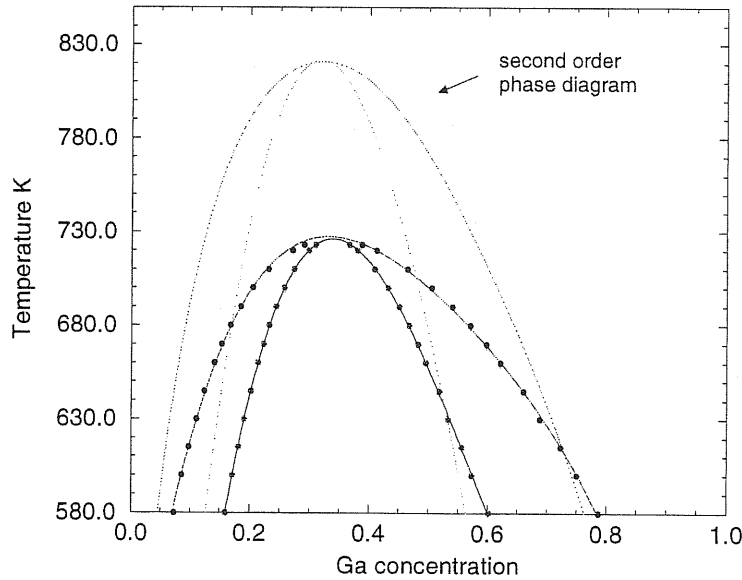


Figure 4.4: Comparison between phase diagrams obtained including and excluding third order terms.

The difference in T_c is about 100 K while the x_c is still unchanged.

4.3 Conclusions

Our purpose was to verify the influence of third order terms which in this case were about 10% of the configurational energy, on the final phase diagram, setting up all the machinery to extract them and to include these terms in the Monte Carlo simulations. Indeed, the phase diagram has changed, and the critical temperature is decreased of about 100 K (11%).

We expected to improve second order results, getting closer to the critical parameters experimentally determined; on the contrary, the discrepancy is increased.

Given that the energetics is now nearly exact, we could be induced to think that there is some important feature that we are missing with our approximations (thermal expansion, for example).

Nevertheless, we have to remember that we are considering a system in its thermodynamical equilibrium, but this can be very difficult to obtain experimentally, because the system can fall trapped into a metastable state, so it's difficult to have experimental data which we can rely on.

What we should do is to reproduce the experimental systems, studying the growth of such alloys. However, this would require a different approach, including some sort of dynamics, which is beyond the aim of the present work.

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