THE STRUCTURE DEPENDENT

ELECTRONIC ENERGY OF ALLOYS

GARY ROONEY

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ABSTRACT

GARY ROONEY

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The pseudopotential theory expression for the band structure energy of an alloy is generalized to the ternary alloy case, and it is seen that the binary alloy expression or an expression for a particular structure is a special case of this general formula. The merits of applying pseudo-potential theory to the alloy problem are discussed. The range of applicability of the theory is investigated regarding the use of second order perturbation theory. The validity of this second order perturbation expression is seen to be limited to certain types of alloys.

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CHAPTER 1

INTRODUCTION

The pseudopotential method was first used for elemental crystals. A consistent perturbation theory expansion of the electron energy in a metal, to second order in the potential, yielded a simple approximate expression for the structure dependent conduction electron energy (1) and (2). The method was used extensively for the investigation of electronic band structure and understanding electronic properties in crystals, as well as sensitive calculations on the variation of axial ratios and structure among the simple metals (3). Since the pseudopotential is smaller than the real potential, the accuracy of the perturbation expression is increased by using it.

The first attempts to extend the theory to compounds utilized the emperical pseudopotential method (4). The emperical pseudopotential method obtains the pseudopotential or matrix elements of the pseudopotential by interpreting experimental data and adjustment to observed band structure. This fitting of the pseudopotential to optical and other data is convenient for elements and perfectly ordered compounds because only a few matrix elements need be evaluated. The matrix element, taken as a function of the wave vector, is evaluated only at the first few reciprocal lattice vectors. Thus the values of these matrix elements could be taken as adjustable parameters of the theory. This method automatically overcomes a number of theoretical and computational problems but it also obscures much of the physics involved and is not capable of determining the effects of disorder in an alloy. Also, since the screening potential and the ionic pseudopotential

are not seperated in the emperical pseudopotential method, the bare ionic pseudopotentials are not known. Transferability of ionic pseudopotentials is an important concept in the study of alloys and the emperical pseudo-potential method does not permit this.

To account for the effects of disorder and to gain fundamental insight into the alloy problem the matrix elements of the ionic pseudopotential must be known for at least the lower part of the quasi-continuum of wave vector space, and be a function of ionic properties only. A first principles pseudopotential can be obtained from atomic wave functions (5), and Hayes (6) was the first to use these ionic pseudopotential matrix elements to obtain an energy expression for a binary alloy with random order. The model potential of Heine and Abarenkov (7) and its subsequent optimization by Shaw (8) has largely replaced the pseudopotential computed from atomic wave functions. In the model potential a simple square well of depth A inside some model radius R_m and the appropriate Coulomb potential outside is used to describe the potential.

$$V_{ps}^0 = \sum_{\ell} A_\ell (\epsilon) P_\ell \qquad r < R_m$$
$$= -\frac{Z}{r} \qquad r > R_m$$

This is the pseudopotential of the bare ion core of charge Z to which has to be added the potential from the conduction electrons. The well depth A can be adjusted so that the spectroscopically observed energy levels of one electron added to the ion are reproduced. A depends on the angular momentum and P_ℓ is the projection operator which picks out the component of the total wave function of the electron. The A_ℓ's depend slightly on the energy of the scattered electron and the matrix elements between plane waves are non-local operators. Because spectroscopically observed energy values for one extra electron in

the ionic potential are used, the fitting automatically includes all self-consistancy in the core and exchange and correlation between the outer electrons and the core.

Although the parameters of the model potential are experimentally derived, they are quantities which characterize the bare ionic potential alone; the data used is atomic and not solid state data. The bare model potential is largely independent of its environment and the transferability of the model potential, which is basic to the study of alloys, is applicable (9). Since we ultimately wish to understand the properties of solids in terms of the basic properties of atoms no physical insight is lost by using model-potentials because only atomic data is obtained experimentally. It is for these reasons that recent theoretical work and calculations concerning alloys have used model potential (9 - 1?).

The formal structure of the theory as applied to electronic structure of an alloy does not depend on the type of pseudopotential used. The method was chiefly initiated by Harrison (5) and Hayes (6). Because the pseudopotential is small, within certain restrictions Phillips (13), and the electron screening is linear (14 - page 51), perturbation theory allows the breakdown of the entire crystal pseudopotential into the sum of ionic pseudopotential of the individual ions. The matrix elements are broken up into structure factors and form factors. The form factors are independent of position and approximately independent of their environment. Since a basic quantity of the theory, the form factors, is approximately independent of the concentration and degree of order, pseudopotential theory is useful in the study of alloys.

Recent developments in the theory have been mainly concerned with improving the approximations involved such as the change in screening with concentration and the small changes in the ionic model potentials as the

environment changes (9) (15). These improvements are obvious in general and merely provide more accuracy in calculations. Kogachi (11) has succeeded in incorporating the effects of short range order into the structure dependent electronic energy expression, while Phillips (16) has modified pseudopotential theory to include covalently bonded structures although it has not yet been applied to covalently bonded alloys.

Model potential theory has been applied to binary alloys recently by several authors. Inglesfield (17) explained the tendency for intermediate compounds to be ordered in systems with large electronegativity difference and predicted the phases of three alloy systems. Phase changes of disordered alloys with composition in two binary systems were calculated by Kogachi and Matsuo (12). Ordered phases of several systems were explained successfully by Kogachi (11) using the model potential method. The total energy of thirteen alloys were calculated for different structures in order to predict the actual structure of the alloy, this was done by Matysina (10). Katada et al (18) derived an expression for the structure dependent energy and ordering energy of a hexagonal close packed binary alloy in order to explain the existence of the ordered compounds Mg_3 Cd and $MgCd_3$ in the Mg-Cd system.

With the exception of Richardson (19), who used the emperical pseudopotential method and did not consider the effects of disorder, ternary alloys have not been studied theoritically to any extent. By extending the theory of Harrison (5) and Hayes (6) for the structure dependent energy of an alloy, a general expression will be derived for the structure dependent electronic energy of an alloy as a function of concentration and type of order. This will be done for a binary and ternary alloy. Also the limitations of applying pseudopotential theory to alloys will be examined.

CHAPTER 2

PERTURBATION THEORY

2.1 Application to Elemental Crystals

Following Harrison (1) and Pick and Sarma (2) the energy eigenvalues of electrons in a crystal can be written to second order in the pseudo-potential in atomic units as

$$E(\vec{k}) = \tfrac{1}{2} k^2 + \langle \vec{k} | V(\vec{r}) | \vec{k} \rangle + \sum_{\vec{q}}{}' \frac{|\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle \langle \vec{k} | V(\vec{r}) | \vec{k}+\vec{q} \rangle |}{\tfrac{1}{2} k^2 - \tfrac{1}{2}(\vec{k}+\vec{q})^2} \qquad (2\text{-}1)$$

where $\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle$ are the matrix elements of the crystal pseudopotential between plane waves of wave vector $\vec{k}$ and $(\vec{k} + \vec{q})$. At the band gaps this is a bad approximation for $E(\vec{k})$ however the errors cancel for states just below and above the gap (20 - page 269). Therefore summing $E(\vec{k})$ up to the Fermi surface K_F gives the correct electronic energy to second order. Neglecting the first two terms of (2-1) because they are structure independent gives

$$U_{bs.} = N^{-1} \sum_{k<k_F} \sum_{\vec{q}}{}' \frac{\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle \langle \vec{k} | V(\vec{r}) | \vec{k}+\vec{q} \rangle}{\tfrac{1}{2} k^2 - \tfrac{1}{2}(\vec{k}+\vec{q})^2} \qquad (2\text{-}2)$$

U_{bs} is the structure dependent electronic energy per ion where N is the number of ions and is called the band structure energy. The Fermi surface is taken as spherical since differences in summing over the true Fermi surface and the Fermi sphere are of third order (5 - page 38).

Because the pseudopotential is the sum of potentials centered on the ion sites the matrix elements of the total pseudopotential can be factored.

$$\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle = (N\Omega_0)^{-1}\int e^{-i(\vec{k}+\vec{g})\cdot\vec{r}}\sum_{j}\nu(\vec{r}-\vec{r_j})e^{i\vec{k}\cdot\vec{r}}\,d^3\vec{r}$$

$$= (N\Omega_0)^{-1}\int\sum_{j}e^{-i\vec{g}\cdot\vec{r_j}}e^{-i(\vec{k}+\vec{g})\cdot(\vec{r}-\vec{r_j})}\nu(\vec{r}-\vec{r_j})e^{+i\vec{k}\cdot(\vec{r}-\vec{r_j})}\,d^3\vec{r}$$

$$= N^{-1}\sum_{j}e^{-i\vec{g}\cdot\vec{r_j}}\,\Omega_0^{-1}\int e^{-i(\vec{k}+\vec{g})\cdot\vec{r}}\nu(\vec{r})e^{i\vec{k}\cdot\vec{r}}\,d^3\vec{r}$$

$$=\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle = N^{-1}\sum_{j}e^{-i\vec{g}\cdot\vec{r_j}}\langle \vec{k}+\vec{g}|\nu(r)|\vec{k}\rangle$$

where Ω_0 is the atomic volume

and $\nu(\vec{r})$ is the screened ionic pseudopotential.

$$\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle = S(\vec{g})\langle \vec{k}+\vec{g}|\nu(r)|\vec{k}\rangle \qquad (2\text{-}3)$$

Thus the matrix elements of the pseudopotential factor into a part
depending only on the ion positions, called the structure factor, and a
part depending on only the individual ionic potentials, called a form factor.
This is an essential part of the pseudopotential theory of crystals and
is extremely important when generalizing the theory to alloy crystals.

The total crystal pseudopotential is actually the ionic potentials
plus the potential due to the conducting electrons. If the conduction
electron density is approximately uniform, and it is calculated only to
first order, its effect is to screen the ionic pseudopotentials.

The matrix elements of the total crystal potentials can be written
for a local potential.

$$\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle = \langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle/\epsilon(\vec{g}) \qquad (2\text{-}4)$$

where $V(\vec{r})$ is the bare crystal pseudopotential (5). $\epsilon(q)$ is the screening factor or dielectric function. The calculation of $\epsilon(q)$ by simple perturbation theory can take into account correlation and exchange in different ways (21) but the usual Lindhard dielectric function is

$$\epsilon(\vec{q}) = 1 - \left(\frac{6\pi}{\Omega_0 q^2}\right) \chi(\vec{q})$$

$$\chi(\vec{q}) = N^{-1} \sum_{k < k_F} \left[\tfrac{1}{2}k^2 - \tfrac{1}{2}(\vec{k}+\vec{q})^2 \right]^{-1}$$

From (2-3) and (2-4) the matrix elements of the crystal pseudopotential can be written as

$$\langle \vec{k}+\vec{q} | M(r) | \vec{k} \rangle = S(\vec{q}) \frac{\langle \vec{k}+\vec{q} | v(r)^{ion} | \vec{k} \rangle}{\epsilon(q)}$$

where

$$\frac{\langle \vec{k}+\vec{q} | v(r)^{ion} | \vec{k} \rangle}{\epsilon(q)} = \langle \vec{k}+\vec{q} | v(r) | \vec{k} \rangle = v(q)$$

and $v(r)^{ion}$ is the unscreened ionic pseudopotential.

The total energy is not just the sum of the one electron energies because in a self-consistent field theory the electrostatic self-energy of the electron system is counted twice. It must be subtracted to give the band structure energy per ion.

$$U_{bs} = N^{-1} \sum_{\vec{q}}' |S(\vec{q})|^2 v(\vec{q})^2 \sum_{k < k_F} \left[\tfrac{1}{2}k^2 - \tfrac{1}{2}(\vec{k}+\vec{q})^2 \right]^{-1} - \tfrac{1}{2}\Omega_0 \sum_{\vec{q}} \rho(q) V^{sc}(\vec{q})$$

where $V^{sc}(q)$ is the screening potential of the electron gas and $\rho(q)$ the electron charge density.

For a local potential $V^{sc}(q)$ is $S(q)\,v(q)\,(1-\epsilon(q))$ and $\rho(\hat{q}) = 2\,\Omega_o^{-1}\,v(q)\,\chi(q)$ (20 - page 272)

giving

$$U_{bs} = \sum_q{}' \, |S(q)|^2 \, |v(q)|^2 \, \chi(q) \, \epsilon(q) \qquad (2\text{-}5)$$

where $\langle \vec{k}+\vec{q} | v(\vec{r}) | \vec{k} \rangle \langle \vec{k} | v(\vec{r}) | \vec{k}+\vec{q} \rangle = |v(q)|^2$ for a local pseudopotential.

Equation (2-5) gives the band structure energy for an elemental crystal in the local approximation.

$$S(\vec{q}) = N^{-1} \sum_j e^{-i\vec{q}\cdot\vec{r}_j} = n^{-1} \sum_\alpha e^{-i\vec{q}\cdot\vec{r}_\alpha} \qquad \text{for an element.}$$

where n is the number of ions per unit cell and $\vec{r}_\alpha$ the positions within the unit cell.

When an elemental crystal is considered $S(\vec{q}) = 0$, when $\vec{q}$ is not a reciprocal lattice vector $\vec{g}$. The general expression for the band structure energy of an elemental crystal is then,

$$U_{bs} = \sum_q{}' \, |S(q)|^2 \, |v(q)|^2 \, \chi(q) \, \epsilon(q) \qquad (2\text{-}6)$$

$|S(\vec{q})|^2$ is calculated for different structures according to Harrison (5), for instance.

2.2 Application to Alloy Crystals

The simple binary alloy was first treated by Harrison (5). The band structure energy can still be written in the form

$$U_{bs} = \sum_{\vec{q}}{}' |\langle \vec{k}+\vec{q} | V^{\circ}(\vec{r}) | \vec{k} \rangle|^2 \, \tilde{\chi}(q) \, \epsilon^{-1}(q) \qquad (2\text{-}7)$$

but no such factorization of the matrix elements as in equation (2-3) is possible, because of the two different atomic potentials involved in $V^{\circ}(\vec{r})$ the unscreened crystal pseudopotential.

The unscreened crystal potential must be written as

$$V^{\circ}(\vec{r}) = \sum_{i} v_A^{ion}(\vec{r}-\vec{r}_i) + \sum_{j} v_B^{ion}(\vec{r}-\vec{r}_j)$$

where $\vec{r}_i$ and $\vec{r}_j$ are lattice vectors.

This is a simple lattice of one atom per unit cell.

Taking the matrix elements of this alloy potential, equation (2-3) is generalized to

$$\langle \vec{k}+\vec{q} | V^{\circ}(\vec{r}) | \vec{k} \rangle = N^{-1} \sum_{i}^{N} e^{-i\vec{q}\cdot\vec{r}_i} \langle \vec{k}+\vec{q} | v_A^{ion}(\vec{r}) | \vec{k} \rangle$$
$$+ N^{-1} \sum_{j}^{N_B} e^{-i\vec{q}\cdot\vec{r}_j} \langle \vec{k}+\vec{q} | v_B^{ion}(\vec{r}) - v_A^{ion}(\vec{r}) | \vec{k} \rangle \qquad (2\text{-}8)$$

There are now two structure factors in the matrix element.

$$N^{-1} \sum_{i}^{N} e^{-i\vec{q}\cdot\vec{r}_i}$$

sums over all ions sites just as the structure factor of a pure metal. If $\vec{q}$ is a reciprocal lattice vector of the basic crystal structure, $\vec{g}$, this first structure factor will be unity, otherwise zero.

The second structure factor $N^{-1} \sum_{d}^{N_\beta} e^{-i\vec{q}\cdot\vec{r}_d}$ is equal to C_β, the ratio of B atoms to the total number of atoms, if $\vec{q}$ is a reciprocal lattice vector, however it is in general non-zero for other values of $\vec{q}$.

Thus we have for $\vec{q} = \vec{g}$

$$\langle\vec{k}+\vec{g}|V^o(\vec{r})|\vec{k}\rangle = C_A\langle\vec{k}+\vec{g}|V_A^{ion}(\vec{r})|\vec{k}\rangle + C_\beta\langle\vec{k}+\vec{g}|V_B^{ion}(\vec{r})|\vec{k}\rangle$$

If $\vec{q} \neq \vec{g}$ then (2-8) has the form

$$\langle\vec{k}+\vec{g}|V^o(\vec{r})|\vec{k}\rangle = S'(q)\langle\vec{k}+\vec{g}|V_B^{ion}(\vec{r})-V_A^{ion}(\vec{r})|\vec{k}\rangle$$

where $S(q) = N^{-1} \sum_{d}^{N_\beta} e^{-i\vec{q}\cdot\vec{r}_d}$

The band structure energy for an alloy is now

$$U_{bs} = \sum_{\vec{g}}' \left[C_A \widetilde{V_A(g)} + C_\beta V_B(g)\right]^2 \chi(g)\,\epsilon(g)$$

$$+ \sum_{\vec{q}\neq\vec{g}}' \left[S'(q)\right]^2 \left[V_B(q) - V_A(q)\right]^2 \chi(q)\,\epsilon(q)$$

<div align="right">(2-9)</div>

The structure factor $S'(q)$ is a function of concentration, degree of order and type of structure. All information as to how the two types of ions are situated is contained in $S(\vec{q})$. This structure factor was calculated by Harrison (5) for a random binary alloy of one atom per unit cell. Hayes (6) used this simple theory of a random alloy, together with non-local effects to calculate the ordering energy of LiMg.

From the theory of Harrison (5) the matrix elements of the total crystal potential are seen to divide into two categories. Matrix elements with $\vec{q} = \vec{g}$ a reciprocal lattice vector and matrix elements with $\vec{q} \neq \vec{g}$. The structure factor part of the second type of matrix element must be calculated and contains all information as to how the different ions are

situated in the crystal.

The essential feature of the above theory is the dividing of the sum over $\vec{q}$ for the band structure energy into a sum over the average of the ionic form factors $(C_A V_A(\vec{q}) + C_B V_B(\vec{q}))^2$ and a sum over the difference of these ionic form factors. This is not possible in general. It is made possible by the absence of cross terms when squaring the matrix elements (2-8) to derive (2-9). Inglesfield (22) has shown that this is the case when all sites in the crystal are equivalent. Therefore in generalizing pseudopotential theory to the alloy case, the structural aspects or generalizations to the structure factor part of the matrix elements have restricted somewhat its use. The other part of the matrix elements, the form factors become either averages or differences of the form factors of the ionic constituents.

2.3 Form Factors

In the application of pseudopotential theory, the use of second order perturbation theory, a pseudopotential must be constructed for ionic constituents. If this pseudopotential is constructed from first principles, the result will be a non-local operator and also will depend on the energy of the electron being scattered. The matrix elements of the pseudopotential will be non-local operators (20 - page 319). For many pseudopotentials the nonlocal part is not very great and an approximation known as the "On the Fermi Surface" approximation is used. The form factors are then a function of only one variable q, the wave vector. The effects of using this approximation is discussed by Heine and Weaire (20) and the situation could be improved somewhat by the quasi-local approximation and use of an effective mass (3). In the alloy case the local approximation is especially

convenient since it is the non-local part of the form factor which changes on alloying. These changes however can be determined as by Gupta (15) and Taut and Paasch (9). The error introduced by the local approximation differs with the quantity calculated and the amount of error is not yet known (20 - page 324).

The functional simplicity of the local pseudo-or model potential makes computational difficulties minimal. Because of the small number of parameters local potentials can be applied to a large number of materials and problems and trends can be seen in these parameters. Simple physical models have been produced from pseudopotential theory by the use of local potentials. In the light of recent calculations (10 - 12) it is apparent that local model potentials can also produce at least consistent numerical results. Unscreened local form factors, when used in alloy calculation need only be renormalized to the correct atomic volume by the relation $V_A(q) = \frac{\Omega}{\Omega_A} V(q)$, where Ω and $V(q)$ are the elemental atomic volume and form factor. Fermi surface changes need not be considered in the renormalizing because form factor are generally plotted against $q/2k_F$. In dealing with the structure dependent electronic energy, the band-structure energy, the atomic volume will be treated as a parameter, independent of the structure dependent electronic energy. The atomic volume is determined mainly by the larger free electron energy which is first order in the pseudopotential while the band-structure energy is second order in the pseudopotential. The atomic volume of the alloy can be taken to follow Vangard's Law, to vary linearly with concentration or taken from experimental data. Appreciable error is not likely to occur from small inaccuracies in atomic volume (20 - page 447).

In order to set up a self-consistent potential the bare ionic

pseudopotentials must be screened by the conduction electrons. The conduction electron charge density is calculated only to lowest order in the pseudopotential. This linear approximation enables each Fourier component of the bare pseudopotential to be screened seperatly, $U(q) = \dfrac{V^{ion}(q)}{\epsilon(q)}$ where $V^{ion}(q)$ is the bare local form factor and $\epsilon(q)$ is the appropriate screening factor. There are several forms of $\epsilon(q)$ in use. Some take into account in an approximate way the exchange and correlation of the conduction electrons (20 - page 305). When these screening functions are used in the screening of an ionic pseudopotential in an alloy it is assumed that the valence electrons of each component of the alloy has gone into a uniform distribution of the electron gas. With this assumption the parameters of the dielectric function, the Fermi wave number and the atomic volume can be functions of concentration and $\epsilon(q)$ can be made a function of concentration (12).

CHAPTER 3

THE BAND STRUCTURE ENERGY OF ALLOYS

3.1 The Crystal Pseudopotential

The preceeding theory is now applied to a ternary alloy. The unit cell is allowed to remain arbitrary, inasmuch as the number of atoms and type of atoms in cell are not specified. To second order in the pseudo-potential the structure dependent electronic energy is given by

$$U_{bs} = N^{-1} \sum_{k < k_f} {\sum_{\vec{q}}}' \frac{\langle \vec{k} + \vec{q} | V(\vec{r}) | \vec{k} \rangle \langle \vec{k} | V(\vec{r}) | \vec{k} + \vec{q} \rangle}{\frac{1}{2} k^2 - \frac{1}{2} (\vec{k} + \vec{q})^2}$$

$$- \frac{1}{2} \bar{\Omega}_0 \sum_{\vec{q}} \rho(q) V^{sc}(q) \qquad (3\text{-}1)$$

where $V(\vec{r})$ is the pseudopotential of the entire crystal.

From Chapter 2 and using the "On the Fermi Surface" approximation (3-1) can be written as

$$U_{bs} = {\sum_{\vec{q}}}' |\langle \vec{k} + \vec{q} | V(\vec{r}) | \vec{k} \rangle|_0^2 \chi(q) \epsilon'(q) \qquad (3\text{-}2)$$

$V^0(\vec{r})$ is the unscreened pseudopotential of the entire ionic arrangement, which we must now set up. We assume a substitutional ternary alloy on a perfect lattice. The atomic potentials are localized and nearly spherical around each nucleus. The atomic volume is taken to be equal for each atom and is the weighted average of the elemental atomic volumes.

If we consider a perfectly ordered state of this alloy, within the unit cell there will be sites on which only A atoms will lie and so on

for B and C type atoms. The sites on which A atoms lie are called primary sites and secondary and ternary for B and C atoms respectively. We choose the same primary site from each unit cell to form a lattice. The crystal lattice will be a lattice with a basis. The sites within the cell will be associated with the lattice point by basis vectors. In choosing a unit cell, we cannot do so in the same manner as choosing a unit cell for an elemental crystal. The unit cell must contain at least as many sites as there are kinds of sites. This is done to enable the type of ordering to be described within the unit cell.

N = number of atoms in the crystal

n = number of atoms per unit cell

p = number of primary sites per unit cell

s = number of secondary sites per unit cell

t = number of ternary sites per unit cell

$\vec{\delta}_p^{(1)} \ldots \vec{\delta}_p^{(p)}$ are vectors to primary sites within unit cell with $\delta_p^{(1)} = 0$

$\vec{\delta}_s^{(1)} \ldots \vec{\delta}_s^{(s)}$ are vectors to secondary sites within unit cell with $\delta_s^{(1)} \neq 0$

$\vec{\delta}_t^{(1)} \ldots \vec{\delta}_t^{(t)}$ are vectors to ternary sites within unit cell with $\delta_t^{(1)} \neq 0$

These vectors are constant within the crystal, even if a change of order or composition is experienced. This is so because the vectors refer to the type of site and not the kind of atom that happens to occupy the site.

N_A^P = number of A atoms on primary sites

N_A^S = number of A atoms on secondary sites

N_A^t = number of A atoms on ternary sites

With similar definitions for N_B^P, N_C^S etc...

$\vec{r}$ with a subscript refers to a lattice point.

These numbers N_A^i are functions of concentration and degree of order. In the completely disordered state N_A^P is not $C_A N$ because the chances of

it taking up a primary site are the same as the chances of it taking up a secondary site if the number of primary sites and secondary sites are the same.

An alloy system may have several perfectly ordered phases, each with a different type of ordering, through its range of concentration. At concentration around these stoichiometric ratios the type of ordering of that compound must be used.

The unscreened pseudopotential $V^o(\vec{r})$ can be written as the sum of ionic pseudopotentials $\nu(\vec{r_i})$ centered at the ionic positions. The crystal potential set up here will be for a crystal of unspecified order. In this way the degree of order can be imposed latter through the N_α^l . If for example A atoms are on secondary sites they are assumed to be equally distributed over all secondary sites.

The unscreened crystal pseudopotential is

$$V^o(\vec{r}) = \sum_{p,s,t} \sum_{(\nu)=1}^{(p)(s)(t)} \sum_{i}^{N_A} \nu^A(\vec{r}-\vec{r_i}+\delta_{p,s,t}^{(\nu)}) + \sum_{\gamma=1}^{(p)} \sum_{j}^{N_\beta^p} \nu_\beta(\vec{r}-\vec{r_j}+\delta_p^{(\nu)}) - \nu_A(\vec{r}-\vec{r_j}+\delta_p^{(\nu)})$$

$$+ \sum_{\gamma=1}^{(p)} \sum_{m}^{N_d^p} \nu_\beta(\vec{r}-\vec{r_m}+\delta_s^{(\nu)}) \nu_A(\vec{r}-\vec{r_m}-\delta_s^{(\nu)}) + \sum_{\delta=1}^{(t)} \sum_{x}^{N_\beta^t} \nu_\beta(\vec{r}-\vec{r_x}-\delta_t^{(\nu)}) - \nu_A(\vec{r}-\vec{r_x}-\delta_t^{(\nu)})$$

$$+ \sum_{\gamma=1}^{(p)} \sum_{y}^{N_c^p} \nu_c(\vec{r}-\vec{r_y}-\delta_p^{(\nu)}) - \nu_A(\vec{r}-\vec{r_y}+\delta_p^{(\nu)}) + \sum_{\delta=1}^{(s)} \sum_{d}^{N_c^s} \nu_c(\vec{r}-\vec{r_d}+\delta_s^{(\nu)}) - \nu_A(\vec{r}-\vec{r_d}+\delta_s^{(\nu)})$$

$$(3\text{-}3)$$

$$+ \sum_{\gamma=1}^{t} \sum_{f}^{N_c^t} \nu_c(\vec{r}-\vec{r_f}-\delta_t^{(\nu)}) - \nu_A(\vec{r}-\vec{r_f}-\delta_t^{(\nu)}).$$

where $U_A(\vec{r_i})$ is the ionic pseudopotential of an A atom. In writing down the crystal pseudopotential, the A atoms were first taken to be on all sites and then the $U_A(\vec{r_i})$ was subtracted from the sites where an atom different from A was situated. This was done to facilitate the introduction of the structure factor of the entire lattice in the proceeding equations. The sign $\sum_{p,s,t}$ means that all basis vectors are summed over in this first term

$$\sum_{p,s,t} \sum_{\gamma=1}^{(p)(s)(t)} \sum_{i}^{\frac{N}{m}} U_A(\vec{r}-\vec{r_i}-\delta_{p,s,t}^{(\gamma)}) = \sum_{\gamma=1}^{(p)} \sum_{i}^{\frac{N}{m}} U_A(\vec{r}-\vec{r_i}-\delta_p^{(\gamma)}).$$

$$+\sum_{\gamma=1}^{(s)} \sum_{i}^{\frac{N}{m}} U_A(\vec{r}-\vec{r_i}-\delta_s^{(\gamma)}) + \sum_{\gamma=1}^{(t)} \sum_{i}^{\frac{N}{m}} U_A(\vec{r}-\vec{r_i}-\delta_t^{(\gamma)})$$

Taking for instance the second term in (3-3) and particular basis vector, say $\delta_p^{(2)}$ therefore $\gamma=2$ we have

$$\sum_{j}^{\frac{N_B^P}{}} U_B(\vec{r}-\vec{r_j}-\delta_p^{(2)}) - U_A(\vec{r}-\vec{r_j}-\delta_p^{(2)})$$

This is the pseudopotential at $\vec{r}$ due to all B atoms on the second primary site of the unit cells in the crystal. Since there are p primary sites per unit cell the second primary sites will receive only $1/p$ of the total number of B atoms on primary sites. That is the number of B atoms on second primary sites is $\dfrac{N_B^P}{P}$

For the perturbation theory we require the matrix elements between all plane waves allowed by the periodic boundary conditions of the crystal. We will however use the "On the Fermi Surface" approximation and take the matrix elements between only those plane waves whose wave vector $\vec{k}$ lies on the Fermi surface.

$$\langle \vec{k}+\vec{q} | V^o_{(r)} | \vec{k} \rangle = \frac{1}{\Omega_o N} \int_\Omega e^{-i(\vec{k}+\vec{q})\cdot\vec{r}} V^o_{(\vec{r})} e^{+i\vec{k}\cdot\vec{r}} d^3\vec{r} \qquad (3\text{-}4)$$

where $\Omega_o N = \Omega$ the volume of the crystal.

Substituting (3-3) into (3-4) we get

$$\langle \vec{k}+\vec{q} | V^o_{(r)} | \vec{k} \rangle = \sum_{\gamma=1}^{\omega(t)} N^{-1} \sum_i^N V_h(q) e^{-i\vec{q}\cdot(\vec{r}_i + \vec{\delta}^{(\gamma)}_{A,c})}$$

$$+ \sum_{\gamma=1}^{(P)} N^{-1} \sum_j^{N^P_\beta} (V_A(q) - V_h(q)) e^{-i\vec{q}\cdot(\vec{r}_j + \vec{\delta}^{(\gamma)}_P)} + \sum_{\gamma=1}^{(S)} N^{-1} \sum_m^{N^S_\beta} (V_B(q) - V_h(q)) e^{-i\vec{q}\cdot(\vec{r}_m + \vec{\delta}^{(\gamma)}_S)}$$

$$\qquad (3\text{-}5)$$

$$+ \sum_{\gamma=1}^{(t)} N^{-1} \sum_x^{N^t_\beta} (V_\beta(q) - V_h(q)) e^{-i\vec{q}\cdot(\vec{r}_x + \vec{\delta}^{(\gamma)}_t)} + \sum_{\gamma=1}^{(P)} N^{-1} \sum_j^{N^P_c} (V_c(q) - V_h(q)) e^{-i\vec{q}\cdot(\vec{r}_j + \vec{\delta}^{(\gamma)}_P)}$$

$$+ \sum_{\gamma=1}^{(S)} N^{-1} \sum_d^{N^S_c} (V_c(q) - V_h(q)) e^{-i\vec{q}\cdot(\vec{r}_d + \vec{\delta}^{(\gamma)}_S)} + \sum_{\gamma=1}^{(t)} N^{-1} \sum_f^{N^t_c} (V_c(q) - V_h(q)) e^{-i\vec{q}\cdot(\vec{r}_f + \vec{\delta}^{(\gamma)}_t)}$$

with

$$V_A(q) = \frac{1}{\Omega_o} \int e^{-i(\vec{k}+\vec{q})\cdot\vec{r}} V_h(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r}$$

the bare ionic form factor.

Since we have used the "On the Fermi Surface" approximation, we see that the matrix elements of the crystal pseudopotential are functions of q only, where $\vec{q}$ is the difference between all wave numbers that lie on the Fermi surcace. The q's form a quasicontinuous set determined only by the boundary conditions of the crystal. From the theory of Chapter 2 it

is seen that the matrix elements take on a different form when the plane waves differ by a reciprocal lattice vector. It is therefore necessary to obtain a form of (3-5) when $\vec{q} = \vec{g}$ a reciprocal lattice vector, and also when it is not.

3.2 Form of Matrix Elements for $\vec{q} = \vec{g}$

When $\vec{q}$ is a reciprocal lattice vector $\vec{g}$ then

$$\frac{1}{N} \sum_{i}^{N} e^{-i\vec{g}\cdot\vec{r}_i} = \frac{1}{n}$$

since i goes over all lattice points.

Sums of the type

$$\frac{1}{N} \sum_{g}^{N_c^p} e^{-i\vec{g}\cdot(\vec{r}_g + \vec{\delta}_p^{(\gamma)})} = \frac{N_c^p}{pN} e^{-i\vec{g}\cdot\vec{\delta}_p^{(\gamma)}}$$

since g goes over only those lattice points with a C atom on the $\delta_p^{(\gamma)}$ site within that unit cell.

Substituting into (3-5) we get

$$\langle \vec{k} + \vec{g} | V(\vec{r}) | \vec{k} \rangle = \left[\frac{1}{n} \sum_{p,s,t} \sum_{\gamma=1}^{(p)(s)(t)} e^{-i\vec{g}\cdot\vec{\delta}_{p s t}^{(\gamma)}} \right] V_A(g)$$

$$+ \left[\frac{N_B^p}{pN} \sum_{\gamma=1}^{(p)} e^{-i\vec{g}\cdot\vec{\delta}_p^{(\gamma)}} + \frac{N_B^s}{sN} \sum_{\gamma=1}^{(s)} e^{-i\vec{g}\cdot\vec{\delta}_s^{(\gamma)}} + \frac{N_B^t}{tN} \sum_{\gamma=1}^{(t)} e^{-i\vec{g}\cdot\vec{\delta}_t^{(\gamma)}} \right] (V_B(g) - V_A(g))$$

$$+ \left[\frac{N_c^p}{pN} \sum_{\gamma=1}^{(p)} e^{-i\vec{g}\cdot\vec{\delta}_p^{(\gamma)}} + \frac{N_c^s}{sN} \sum_{\gamma=1}^{(s)} e^{-i\vec{g}\cdot\vec{\delta}_s^{(\gamma)}} + \frac{N_c^t}{tN} \sum_{\gamma=1}^{(t)} e^{-i\vec{g}\cdot\vec{\delta}_t^{(\gamma)}} \right] (V_c(g) - V_A(g))$$

where $\sum\limits_{p,s,t}$ in the first term means all sites in the unit cell are summed over.

Collecting the coefficients of each ionic form factor we have from Appendix A

$$\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle = \left[\frac{N_a^p}{pN}\sum_{\delta=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(\delta)}} + \frac{N_a^s}{sN}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(\delta)}} + \frac{N_a^t}{tN}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(\delta)}}\right]V_A(g)$$

$$+\left[N_\beta^p\sum_{\delta=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(\delta)}} + \frac{N_\beta^s}{sN}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(\delta)}} + \frac{N_\beta^t}{tN}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(\delta)}}\right]V_B(g)$$

$$\text{(3-6)}$$

$$+\left[\frac{N_c^p}{pN}\sum_{\delta=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(\delta)}} + \frac{N_c^s}{sN}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(\delta)}} + \frac{N_c^t}{tN}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(\delta)}}\right]V_c(g)$$

The concentration and type of order is inserted into $\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle$ through the N_a^i , which can be expressed as functions of concentration. The matrix elements, when $\vec{q} = \vec{g}$ are seen to depend on the detailed structure of the unit cell because of the presence of the basis vectors.

Sums of the type $\sum\limits_{\delta=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(\delta)}}$ can be evaluated when $\vec{g}$ and δ are put as functions of the lattice parameters.

The summations in (3-6) will in general be different for different $\vec{g}$'s. If the sites are equivalent in the crystal, the sum over $\vec{g}$ of equation (3-6) squared, can be divided into several sums over the different sets of $\vec{g}$'s which give the different forms of (3-6).

One set of $\vec{g}$'s will give a summation over a form of (3-6) squared depending on the potential of the average lattice. Other forms of (3-6) squared to be summed over with the appropriate $\vec{g}$'s will be functions of order and the difference in the ionic pseudopotential of the constituent atoms. The separation of order dependent and ionic pseudopotential parts into separate

factors will be possible only if all sites are equivalent. · The number of different forms of (3-6) squared, will depend on the ordering type involved and the particular degree of order (Appendix B).

The sum over $|\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle|^2$ for all $\vec{g}$'s which is needed in the electronic band structure energy is then

$$\sum_{\vec{g}} \left[C_A V_A(g) + C_B V_B(g) + C_C V_C(g)\right]^2 + \sum_{g'} \left[A'(V_B(g') - V_A(g')) + B'(V_C(g') - V_A(g'))\right]^2$$

$$+ \cdots \sum_{g''} \left[A''(V_B(g'') - V_A(g'')) + B''(V_C(g'') - V_A(g''))\right]^2 \qquad (3\text{-}7)$$

where A'A", B'B" are simple functions of concentration or zero for maximum order and all zero for complete disorder.

3.3   Matrix Elements for $\vec{q} \neq \vec{g}$

On specifying in (3-5) that $\vec{q}$ is not a reciprocal lattice vector, only the first term vanishes, because it has a sum over all lattice points.

$$\sum_{i}^{N_m} e^{-i\vec{g}\cdot\vec{r}_i} = 0 \qquad\qquad \text{for } \vec{q} \neq \vec{g}$$

therefore we have

$$\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle = \sum_{g=1}^{(p)} N^{-1} \sum_{g}^{\frac{N_B^p}{2}} (V_B(g) - V_A(g)) e^{-i\vec{g}\cdot(\vec{r}_g + \vec{S}_p^{(g)})} + \sum_{g=1}^{(g)} N^{-1} \sum_{A}^{\frac{N_B^s}{2}} (V_B(g) - V_A(g)) e^{-i\vec{g}\cdot(\vec{r}_{\vec{k}} - \vec{S}_s^{(g)})}$$

$$+ \sum_{g=1}^{(g)} N^{-1} \sum_{A}^{\frac{N_A^t}{2}} (V_B(g) - V_A(g)) e^{-i\vec{g}\cdot(\vec{r}_{\vec{k}} + \vec{S}_t^{(g)})} + \sum_{g=1}^{(p)} N^{-1} \sum_{}^{\frac{N_C^p}{2}} (V_C(g) - V_A(g)) e^{-i\vec{g}\cdot(\vec{r}_g + \vec{S}_p^{(g)})}$$

$$+ \sum_{g=1}^{(s)} N^{-1} \sum_{C}^{\frac{N_C^s}{2}} (V_C(g) - V_A(g)) e^{-i\vec{g}\cdot(\vec{r}_d + \vec{S}_s^{(g)})} + \sum_{g=1}^{(t)} N^{-1} \sum_{}^{\frac{N_C^t}{2}} (V_C(g) - V_A(g)) e^{-i\vec{g}\cdot(\vec{r}_t + \vec{S}_t^{(g)})} \qquad (3\text{-}8)$$

This is the matrix element for a particular ionic configuration out of all the possible configurations the alloy can have with concentration and degree of order held constant. All information as to how the three types of ions are situated is contained in $\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle$.

Since it is actually the product of the complex conjugated matrix elements we need, we will evaluate $|\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle|^2$.

The actual ionic configuration of a given alloy specimen is not known, only its concentration and degree of order. Therefore we take an average of $|\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle|^2$ over all possible ionic configurations.

It is the averaged value of $|\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle|^2$ that will be used as the matrix elements in expression for the band structure energy.

After multiplying (3-8) by its complex conjugate and averaging each term of this product over all ionic configurations, from Appendix C we have

$$|\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle|^2 = \left[\frac{N_B^p(pN-N_B^p n)}{p N^3} + \frac{N_B^s(sN-N_B^s n)}{s N^3} + \frac{N_B^t(tN-N_B^t n)}{t N^3} \right] (V_B(q) - V_A(q))^2$$

$$- \left[\frac{2N_c^p N_B^p n}{p N^3} + \frac{2N_B^s N_c^s n}{s N^3} + \frac{2N_c^t N_B^t n}{t N^3} \right] (V_B(q) - V_A(q))(V_c(q) - V_A(q))$$

$$\tag{3-9}$$

$$+ \left[\frac{N_c^p(pN-N_c^p n)}{p N^3} + \frac{N_c^s(sN-N_c^s n)}{s N^3} + \frac{N_c^t(tN-N_c^t n)}{t N^3} \right] (V_c(q) - V_A(q))$$

Again, the N_α^i can be expressed as functions of concentration or put equal to zero depending on the ordering. We see that $|\langle \vec{k}+\vec{q} | V(\vec{r}) | \vec{k} \rangle|^2$ does not depend on the structure but on the type of ordering through the ratios $\frac{p}{n}$, $\frac{s}{n}$, $\frac{t}{n}$.

When the alloy is at perfect order for one of its stoichiometric ratios,

$N_A^s = N_A^t = N_B^t = N_B^t = N_c^p = N_c^s = 0$ and $C_A = \frac{p}{n}$, $C_B = \frac{g}{n}$, $C_c = \frac{t}{n}$

the energy due to disorder is zero because $|\langle \vec{k} + \vec{q} | V(\vec{r}) | \vec{k} \rangle|^2$ is zero.

For the simple case of a completely disordered binary alloy of one atom

per unit cell, (3-9) becomes for

$N_B^p = N_B = CN$ and $p = n = 1$.

$$\left(|\langle \vec{k} + \vec{q} | V(r) | \vec{k} \rangle|^2 = \frac{cN(N-cN)}{N^3} \left(v_B(q) - v_A(q) \right)^2 \right.$$

$$= \frac{1}{N} c(1-c) \left(v_B(q) - v_A(q) \right)^2$$

which is Harrison's result

(5 - page 145).

3.4   Band Structure Energy Per Ion

To obtain the band structure energy U_{bs}, of the alloy we substitute
in (3-2) for the matrix elements, because the matrix elements have several
forms depending on the particular wave vector $\vec{q}$ the sum of (3-2) is now
split into several sums over the different sets of $\vec{q}$'s.   The number of
these sums depends on the type of ordering and degree of order.

We first insert into (3-2) the matrix elements corresponding to
reciprocal lattice vectors and obtain sums over the different sets of $\vec{g}$'s
from (3-7), next we insert the form of the matrix elements for $\vec{q}$ not a
reciprocal lattice vector from (3-9).

$$U_{bs} = \sum_{g} F(c,g) + \sum_{g'} [A'G^B_{(g')} + B'G^C_{(g')}]^2$$

$$+ \cdots + \sum_{g''} [A''G^B_{(g'')} + B''G^C_{(g'')}]^2$$

$$+ \sum_{g} f_1(c) G^{B^2}_{(g)} - f_2(c) G^B_{(g)} G^C_{(g)} + f_3(c) G^{C^2}_{(g)}$$

$$(3\text{-}10)$$

where
$$F(c,g) = [c_A V_A(g) + c_B V_B(g) + c_C V_C(g)]^2 X(g) \in^{-1}(g)$$

$$G^B_{(g)} = (V_B(g) - V_A(g)) \sqrt{X(g) \in^{-1}(g)}$$

$$G^C_{(g)} = (V_C(g) - V_A(g)) \sqrt{X(g) \in^{-1}(g)}$$

The A', A", B', B" are simple functions of concentration or zero and must be evaluated for the particular type of order and degree of order in the alloy (Appendix B).

$f_1(c), f_2(c), f_3(c)$ are functions of concentration and degree of order, and type of order and are the coefficient of the ionic pseudopotential form factors in (3-9).

Equation (3-10) gives the band structure energy per ion for a general ternary alloy with all sites equivalent. Equation (3-10) can be reduced to important special cases by removing certain terms of (3-6) and (3-9) in equation (3-10).

Some ternary alloys through certain ranges of concentration have ordered phases with only two kinds of sites. A atoms are on the first kind of site and B and C atoms are arranged randomly on the second kind of site. The general form of $\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle$ equation (3-6) becomes

$$\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle = \left[\frac{N_A^P}{pN}\sum_{\delta=1}^{(P)}e^{-i\vec{g}\cdot\delta_P^{(\delta)}}+\frac{N_A^S}{sN}\sum_{\delta=1}^{(S)}e^{-i\vec{g}\cdot\delta_S^{(\delta)}}\right]U_A(g)$$

$$+\left[\frac{N_B^P}{pN}\sum_{\delta=1}^{(P)}e^{-i\vec{g}\cdot\delta_P^{(\delta)}}+\frac{N_B^S}{sN}\sum_{\delta=1}^{(S)}e^{-i\vec{g}\cdot\delta_S^{(\delta)}}\right]U_B(g)$$

$$+\left[\frac{N_C^P}{pN}\sum_{\delta=1}^{(P)}e^{-i\vec{g}\cdot\delta_P^{(\delta)}}+\frac{N_C^S}{sN}\sum_{\delta=1}^{(S)}e^{-i\vec{g}\cdot\delta_S^{(\delta)}}\right]U_C(g)$$

and $|\langle\vec{k}+\vec{g}|V(r)|\vec{k}\rangle|^2$ equation (3-9) becomes

$$|\langle\vec{k}+\vec{g}|V(r)|\vec{k}\rangle|^2=\left[\frac{N_B^P(pN-N_B^P m)}{pN^3}+\frac{N_B^S(sN-N_B^S m)}{sN^3}\right](U_B(g)-U_A(g))^2$$

$$-\left[\frac{2N_C^P N_B^P m}{pN^3}+\frac{2N_B^S N_C^S m}{sN^3}\right](U_B(g)-U_A(g))(U_C(g)-U_A(g))$$

$$+\left[\frac{N_C^P(pN-N_C^P m)}{pN^3}+\frac{N_C^S(sN-N_C^S m)}{sN^3}\right](U_C(g)-U_A(g))^2$$

These forms of the matrix elements are put into the sums of (3-10).

For a binary alloy equations (3-6) and (3-9) reduce to

$$\langle \vec{k}+\vec{g}\,|V^0_{(r)}|\vec{k}\rangle = \left[\frac{N^P_A}{pN}\sum_{\gamma=1}^{(P)} e^{-i\vec{g}\cdot\delta^{(\gamma)}_P} + \frac{N^S_A}{sN}\sum_{\delta=1}^{(S)} e^{-i\vec{g}\cdot\delta^{(\delta)}_S}\right]\mathcal{U}_A(g)$$

$$+\left[\frac{N^P_B}{pN}\sum_{\delta=1}^{(P)} e^{-i\vec{g}\cdot\delta^{(\delta)}_P} + \frac{N^S_B}{sN}\sum_{\delta=1}^{(S)} e^{-i\vec{g}\cdot\delta^{(\delta)}_S}\right]\mathcal{U}_B(g)$$

and

$$|\langle \vec{k}+\vec{g}\,|V^0_{(r)}|\vec{k}\rangle = \left[\frac{N^P_A(pN-N^P_B m)}{p\,N^3} + \frac{N^S_A(sN-N^S_B m)}{s\,N^3}\right](\mathcal{U}_B(g)-\mathcal{U}_A(g))^2 \qquad (3\text{-}11)$$

For a binary alloy with all sites equivalent

$$U_{bs} = \sum_{\vec{g}} F(c,g) + \sum_{\vec{g}'} A^2 G^2(g') + \sum_{\vec{g}} f(c)\, G^2(g) \qquad (3\text{-}12)$$

with

$$F(c,g) = (c_A\,\mathcal{U}_A(g) + c_B\,\mathcal{U}_B(g))^2 X(g)\,\epsilon^{-1}(g)$$

$$G(g) = (\mathcal{U}_B(g) - \mathcal{U}_A(g))\sqrt{X(g)\,\epsilon^{-1}(g)}$$

A will be zero for complete disorder or $\dfrac{c_A}{s}\displaystyle\sum_{\delta=1}^{(S)} e^{-i\vec{g}\cdot\xi^{(\delta)}}$ for maximum order.

$f(c)$ is the coefficient of $\left(\mathcal{U}_B(g)-\mathcal{U}_A(g)\right)^2$ in (3-11).

A further restriction on (3-6) and (3-9), that they refer to a binary alloy and also have only one primary site per unit cell, will give Matysina's (23) form for $\langle \vec{k}+\vec{g}\,|V_{(r)}|\vec{k}\rangle$, $|\langle \vec{k}+\vec{g}\,|V^0_{(r)}|\vec{k}\rangle|^2$

CHAPTER 4

THE RANGE OF APPLICATION OF THE THEORY

Although replacing the actual potentials of atoms by pseudo-potentials represents in principle an exact transformation of the Schrodinger equation, it does not in itself guarantee the accuracy of second order perturbation theory for the total energy. The pseudopotential $V(\vec{r})$ of the crystal must be small with respect to the Fermi energy E_{fo}, after the absolute level of the bottom of the band has taken as the zero of energy. If $V(\vec{r})$ is not small compared to E_{fo} perturbation theory and linear screening theory is no longer adequate. It is therefore necessary to restrict the use of this form of perturbation theory to the case in which $V(\vec{r})$ is small throughout the crystal in comparison to E_{fo} .

The fact that the pseudopotential of an atom is small compared to the real atomic potential does not mean it is small compared to the kinetic energy of the free electron gas. In fact the matrix elements of an atomic potential in an elemental crystal or an alloy are of the same order as E_{fo} at low values of q. These low q values of the atomic pseudopotentials must not enter the expansion for the crystal potential $V(\vec{r})$ as such, although they may enter when suitably deminished by being multiplied by an appropriate structure factor. In particular, for an arbitrary arrangement of ions, when the expansion for $V(\vec{r})$ calls for a sum over all $\vec{q}$ values, matrix elements enter the sum which are of the same order as E_{fo} . We are therefore required to inspect the crystal pseudopotential $V(\vec{r})$ before r ceeding with a perturbation expansion of the total electronic energy. In order to estimate the limitations of perturbation theory, we

expand the potential of a binary alloy of A and B atoms. The Fourier expansion for a local pseudopotential is

$$V(\vec{r}) = \sum_{\vec{q}} V(q) e^{+i\vec{q}\cdot\vec{r}}$$

$$V(q) = \frac{1}{N\Omega_0} \int V(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r}$$

(4-1)

For simplicity, we will consider a cubic unit cell with two atoms per unit cell of the alloy.

$$V(\vec{r}) = \sum_{p}^{\frac{N}{2}} \mathcal{U}_A(\vec{r}-\vec{r}_p) + \sum_{p}^{\frac{N}{2}} \mathcal{U}_A(\vec{r}-\vec{r}_p-\delta) + \sum_{s}^{N_B} \mathcal{U}_D(\vec{r}-\vec{r}_s-\delta) - \mathcal{U}_A(\vec{r}-\vec{r}_s-\delta)$$

Maximum order is assumed, with B atoms on secondary sites only. δ is the position vector, with origin within the unit cell of the secondary sites.

$$V(\vec{q}) = \frac{1}{N\Omega_0} \int \left\{ \sum_{p}^{\frac{N}{2}} \mathcal{U}_A(\vec{r}-\vec{r}_p) + \sum_{p}^{\frac{N}{2}} \mathcal{U}_A(\vec{r}-\vec{r}_p-\delta) + \sum_{s}^{N_B} \mathcal{U}_D(\vec{r}-\vec{r}_s-\delta) - \mathcal{U}_A(\vec{r}-\vec{r}_s-\delta) \right\} e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r}$$

$$V(\vec{q}) = \frac{1}{N} \sum_{p}^{\frac{N}{2}} e^{-i\vec{q}\cdot\vec{r}_p} \mathcal{U}_A(q) + \frac{1}{N} \sum_{p}^{\frac{N}{2}} e^{-i\vec{q}\cdot\vec{r}_p} \mathcal{U}_A(q) e^{-i\vec{q}\cdot\delta}$$

(4-2)

$$+ \frac{1}{N} \sum_{s}^{N_B} e^{-i\vec{q}\cdot\vec{r}_s} (\mathcal{U}_D(q) - \mathcal{U}_A(q)) e^{-i\vec{q}\cdot\delta}$$

where $\Omega_0^{-1} \int \mathcal{U}_A(\vec{r}-\vec{r}_p) e^{-i\vec{q}\cdot(\vec{r}-\vec{r}_p)} d^3\vec{r} = \mathcal{U}_A(q)$ the screened ionic pseudopotential.

Substituting (4-2) into (4-1) we get

$$V(\vec{r}) = \sum_{\vec{q}} N^{-1} \sum_{p}^{\frac{N}{2}} e^{-i\vec{q}\cdot\vec{r}_p} \mathcal{U}_A(q) e^{+i\vec{q}\cdot\vec{r}} + \sum_{\vec{q}} N^{-1} \sum_{p}^{\frac{N}{2}} e^{-i\vec{q}(\vec{r}_p+\delta)} \mathcal{U}_A(q) e^{+i\vec{q}\cdot\vec{r}}$$

$$+ \sum_{\vec{q}} N^{-1} \sum_{s}^{N_B} e^{-i\vec{q}(\vec{r}_s+\delta)} (\mathcal{U}_D(q) - \mathcal{U}_A(q)) e^{+i\vec{q}\cdot\vec{r}}$$

The reciprocal lattice vectors $\vec{g}$ divide into two types

$\vec{g}'$ for $e^{-i\vec{g}'\cdot\delta} = 1$ and $\vec{g}''$ for $e^{-i\vec{g}''\cdot\delta} = -1$

$$V(\vec{r}) = V_0 + \sum_{\vec{g}'}{}' \bar{v}(g') e^{+i\vec{g}'\cdot\vec{r}} - C_\beta \sum_{\vec{g}''}{}' (v_\beta(g'') - v_A(g'')) e^{+i\vec{g}''\cdot\vec{r}}$$

$$+ \sum_{\vec{g}}{}' \frac{1}{N} \sum_s^{N_\beta} (v_\beta(g) - v_A(g)) e^{+i\vec{g}\cdot(\vec{r}-\vec{r}_s-\delta)}. \qquad (4\text{-}3)$$

The term V_0 may be absorbed into the zero of energy without effecting the perturbation expansion. It is important therefore that the total potential be smooth and have no large fluctuations. Fluctuations in space of the potential can not be absorbed into the zero and must be small. The way in which the atomic pseudopotentials add together, and not so much their individual magnitude is the important criterion.

Figure la shows the way the ionic pseudopotentials overlap in an elemental crystal where perturbation theory is known to work. It can be seen from figure lb that the total pseudopotential is smooth with only small fluctuations, $\ll E_{F_0}$.

In the case of an alloy there are two ways by which Fig. 1 can have fluctuations too great for perturbation theory. Firstly, when the atoms are too far apart, that is when the unit cell becomes rather open and large; as in Fig. 2 and secondly, the atomic potentials can be too unalike, as in Fig. 3. The last three terms in (4-3) must be small compare to E_{F_0} and their magnitudes are affected by the two cases depicted in figures 2 and 3. The magnitude of the second term is affected by the first case, the magnitude of the third term is affected by both cases, and the fourth term is affected by the second case.
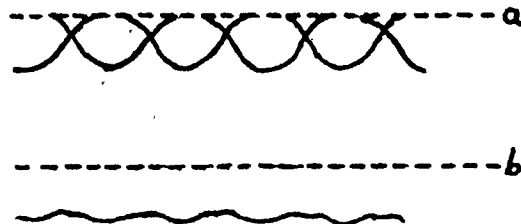
Fig. 1 - Potential in an elemental crystal a) overlaping potentials in close-packed array, b) total potential.

The magnitude of the second term in (4-3) is governed by $\sum_{g'} \bar{v}(g')$ where $\bar{v}(g') = \left(c_A v_A(g') + c_B v_B(g') \right)$, the sum is only over the first few reciprocal lattice vectors, and it is sufficient that each $\bar{v}(g') \ll E_{Fo}$. The curve $\bar{v}(q)$ versus q is typically the same shape as the $v(q)$ curve of an elemental crystal, so there are $\bar{v}(g')$ for which $\bar{v}(g') = O(E_{Fo})$ and also for which $\bar{v}(q) \ll E_{Fo}$, since $\bar{v}(q)$ passes through zero at some point q_o. If the atoms are far apart a large unit cell can produce small $\vec{g}'$ and the corresponding large $\bar{v}(g')$ enters the sum. The volume dependent, structure independent forces are the ones that determine, more or less, the cell volume, because the electron gas is rather incompressible (24). We therefore take the cell size as a parameter.
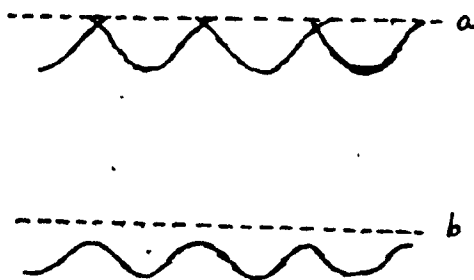
Fig. 2 - a) potentials in an open structured crystal.

b) total potential in an open structured crystal.

From inspection of a typical $\overline{U}(g)$ curve, we see that $\vec{g}$'s lying to the right of q_0 will satisfy $\overline{U}(g) \ll \overline{E}_{F_0}$, but $\vec{g}$'s on the left must be close to q_0 in order to satisfy $\overline{U}(g') \ll E_{F_0}$. To obtain an approximate limitation on the size of the unit cell for/perturbation theory to be trustworthy, we restrict the minimum $\vec{g}'$ of the reciprocal lattice to $g'_{min.} \geq \frac{3}{4} g_0$. From the empty core model (14 - page 55) for $U(g)$ of an atom, we can approximate the value of q_0 for an atom by $q_0 = \frac{\pi}{2R_c}$, where R_c is the radius of the physical atomic core, or the atomic radius when the valence electrons are excluded. Since our $\overline{U}(g)$ is the mean of two atomic form factors, it can be thought of as the matrix elements of a virtual atom with some core radius between the core radius of the constituent atoms. We will assume a cubic unit cell of side a.

Where g'_{mn} for say, body centered cubic, is $\frac{2\pi}{a}(\pm 1/\pm 1/0)$, or any combination of ± 1, ± 1 and 0. Therefore the magnitude of g' is $\frac{2\pi}{a}\sqrt{2}$.

$$g'_{min} \gtrsim \frac{3}{4}\frac{\pi}{2R_c}$$

$$\frac{2\pi\sqrt{2}}{a} \gtrsim \frac{3}{4}\frac{\pi}{2R_c}$$

$$\frac{a}{R_c} \leq 8 \tag{4-4}$$

Although no precise mathematical statement can be made to indicate the breakdown of perturbation theory, from (4-4) we can see that if the cell becomes large or open on the scale of the core radii of the ions, perturbation theory, will be doubtful. A similar requirement should also hold for elemental crystals, since open lattices can lead to fluctuations in the potential, and the first 2 terms in (4-3) are formally the same as the expansion of the potential for an elemental crystal. It is known that perturbation theory fails for elemental covalent crystals, and that covalent structures arise for elements with valence > 4. The volume dependent forces tend to make the unit cell more open at high values of valence, and also the core radius of the ion is small because the high positive charge of the nucleus pulls the core electrons close to it. For these two reasons, mainly the latter, we can expect $\frac{a}{R_c}$ to be large, and therefore perturbation theory would not be a good approximation. For instance, if we apply the requirement $g_{min} \geq \frac{3}{4}\frac{\pi}{2R_c}$ to a face centered cubic or diamond type elemental structure, we obtain

$$\frac{2\pi\sqrt{3}}{a} \leqslant \frac{3}{4}\frac{\pi}{2R_c} \qquad \text{or} \qquad \frac{a}{R_c} \leqslant 9$$

Thus for Silicon we have $\frac{a}{R_c} = 14.8$ and perturbation theory is not a good approximation (20 - page 357).

On the other hand, Aluminum has a value of $\frac{a}{R_c} = 5.95$ and has been the object of many successful calculations using perturbation theory (14 - page 119).
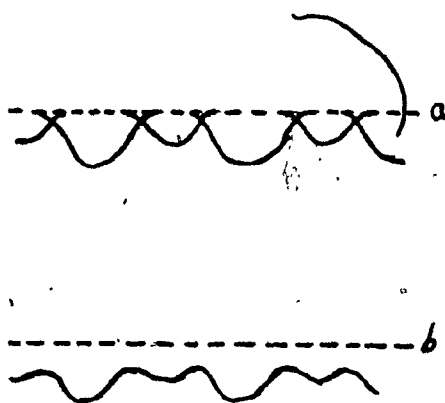

Fig. 3 - a) potentials for two different atoms in an alloy crystal.

   b) total potential in the alloy crystal.

The magnitude of the third term in (4-3) is governed mainly by the difference in the form factors of the constituent atoms. This increases at low q, but the restriction of (4-4) puts a limitation on the length of the $\vec{g}''$,

of the third term. Since the minimum length put on the $\vec{g}'$ in term number two was $3/4\ q_\bullet$ and those $\vec{g}$'s are $\frac{2\pi}{a}\sqrt{2}$, then the minimum on the present g's is $1/2\ q_0$ since they are $\frac{2\pi}{a}\times 1$. The difference in $\mathcal{U}(g)'s$ at this region which is the maximum for $\Delta\mathcal{U}(g'')=\mathcal{U}_B(g'')-\mathcal{U}_A(g'')$ within the allowable length of the $\vec{g}$'s must be small in order to make term number 3 small compared to E_{FO} . Again, it is sufficient for each $\Delta\mathcal{U}(g'')$ to be small for the term to be small because the sum goes over only the first few reciprocal lattice vectors of this type.

For most elements the curves $\mathcal{U}(g)$ versus (q) passes through zero at approximatly the same point q_0 , there being a slight increase in q_0 with increasing valence. The points $\mathcal{U}(0)$ for atoms in an alloy is dictated by its valence. In an alloy the limit of the bare pseudopotential form factor of atom A is given by $\mathcal{U}_A^{ion}(g)\underset{g\to 0}{=}-\frac{4\pi Z_A}{\bar{\Omega}_\bullet g^2}$ where $\bar{\Omega}_\bullet$ is the atomic volume of the alloy and Z_A is the valence of the A atom. The limit of the screening factor is (20 - page 272) $\epsilon_{AB}(g)\underset{g\to 0}{=}-\frac{8\pi}{\bar{\Omega}g^2}\times\chi_{AB}(g)\underset{g\to 0}{=}+\frac{6\pi}{\bar{\Omega}g^2}\bar{Z}\bar{E}_{FO}^{-1}$.

where $\bar{Z}$ is the mean valence and $\bar{E}_{FO}=\frac{\hbar}{2}\bar{k}_F$ is the Fermi energy of the alloy. Therefore $\mathcal{U}_A(0)=\frac{\mathcal{U}_A^{ion}(g)}{\underset{g\to 0}{\epsilon_{AB}(g)}}=-\frac{2}{3}\frac{Z_A}{\bar{Z}}\bar{E}_{FO}$

In the region $1/2\ q_\bullet$, the function $\mathcal{U}_A(g)$ is approximatly linear in q and the slope depends on $-\frac{2}{3}\frac{Z_A}{\bar{Z}}\bar{E}_{FO}$. So we let $\mathcal{U}_A(g)$ around $1/2\ q_\bullet$ be

$$\mathcal{U}_A(g)\approx\frac{2}{3}\frac{Z_A}{\bar{Z}}\bar{E}_{FO}\frac{q}{g_0}-\frac{2}{3}\frac{Z_A}{\bar{Z}}\bar{E}_{FO}$$

and

$$\mathcal{U}_B(g)\approx\frac{2}{3}\frac{Z_B}{\bar{Z}}\bar{E}_{FO}\frac{q}{g_0}-\frac{2}{3}\frac{Z_B}{\bar{Z}}\bar{E}_{FO}$$

Letting $V_A(q)$ approximate a straight line with slope $\dfrac{2}{3}\dfrac{Z_B}{\bar{Z}}\bar{E}_{fo}$ and

putting q_o as the zero point of both $V_A(q)$ and $V_B(q)$ is useful in a

qualitative discussion, since only basic parameters of the individual atoms

describe the form factor.

By evaluating $V_A(q)$ and $V_B(q)$ at $1/2\ q_o$, and subtracting, we obtain an

expression for the maximum value of $\left(V_B(q'') - V_A(q'')\right)$ that ought to

occur in term number 3 of (4-3). Since term number 3 is multiplied by C

we multiply each term $\left(V_B(q'') - V_A(q'')\right)$ by C_B.

To obtain a limitation on the difference in the pseudopotential, we note

that each $C_B\,\Delta V(q'')$ in the third term must be small compared to $\bar{E}_{fo}$

Putting $\Delta V(q'')$ an order of magnitude less than $\bar{E}_{fo}$

$$C_B\,\Delta V(\tfrac{1}{2}q_o) \leq .1\,\bar{E}_{fo}$$

$$C_B/3\ \bar{E}_{fo}/\bar{Z}\ (Z_A - Z_B) \leq .1\,\bar{E}_{fo}$$

$$(Z_A - Z_B) \leq .23\ Z_A/C_B \tag{4-5}$$

Noting that $\bar{Z} = Z_A(1 - C_B) + Z_B\,C_B$

From (4-5) we see that, unless the concentration of one atomic type is small,

a valence difference of more than one will most likely invalidate perturbation

theory, even if condition (4-4) is satisfied. Alloys of atoms with valence

one and two seem doubtful, but the approximations made in arriving at

(4-5) are less accurate for these atoms and tend to overestimate the

difference in $V_A(q'')$ and $V_B(q'')$. Therefore, alloys of atoms with valence

one and two are able to be studied by perturbation theory if condition

(4-4) is satisfied.

The last term in equation (4-3) can be changed to an integral by the relation (20 - page 276)

$$N^{-1} \sum_{\vec{q}} \Rightarrow \frac{\bar{\Omega}_0}{2\pi^3} \int d^3\vec{q}$$

The last term in (4-3) then becomes

$$\sum_{s}^{N_B} \frac{\bar{\Omega}_0}{2\pi^3} \int e^{+i\vec{q}\cdot(\vec{r}-\vec{r}_s-\vec{\delta})} \left(\nu_B(q) - \nu_A(q)\right) d^3\vec{q}$$

In spherical coordinates it becomes

$$\sum_{s}^{N_B} \frac{\bar{\Omega}_0}{2\pi^3} \int_0^{2\pi} \int_0^{\pi} \int_0^{3K_f} e^{-iq(r-r_s-\delta)\cos(\theta-\theta')\cos(\phi-\phi')} \Delta\nu(q)\, q \sin\theta\, d\theta\, d\phi\, dq$$

where θ', ϕ' are the coordinates of the vector $(\vec{r} - \vec{r}_s - \vec{\delta})$ and θ and ϕ are the coordinates of $\vec{q}$.

The magnitude of this term depends on the concentration and on

$$\bar{\Omega}_0 \int_0^{3k_f} q^2\, \Delta\nu(q)\, dq$$

Again, it can be seen from (4-6), that the difference in the form factors must be small in order that the whole last term of equation (4-3) be small. In this case, however, the difference in form factors is considered at all values of q below a cutoff of about $3k_f$. In considering an alloy of atoms of different valences, the bulk of (4-6) comes from low q values. The q = 0 points of the $\nu_A(q)$ and $\nu_B(q)$ curves are therefore important, and must

be close together to make $\Delta U(q)$ small at this low region of q. The smaller the valence difference, the smaller the last term in equation (4-3) will be. Since there is already a restriction on the valence difference by condition (4-5), that is the valence difference must be zero or one except possibly at low concentrations where a valence difference of two might suffice, the last term in (4-3) will have the same restriction.

While in applying pseudopotential perturbation theory each case must be considered according to its mertis, the criterion set up above, though not mathematically precise, indicates types of structures and, constituent atoms that are favorable and unfavorable to perturbation theory. Metallic alloys ($Z \leqslant 3$) seem most trustworthy. They are close packed structures of atoms with the same valence or a difference of one or two. Here linear screening is a good approximation and the close packed structure makes the crystal potential smooth. Z.A. and E.A. Matysina (10) have successfully substantiated the structure of 11 of 13 metallic alloys by the pseudopotential method. They failed however, in an attempt to substantiate the structure of the alloy Li-50% Al, indicating that a valence difference of 2, at intermediate concentration, is not favorable to perturbation theory. However, the structure of Li-95% Al was substantiated, indicating that, at least for metallic alloys, a valence difference of 2, at low concentration, might not invalidate perturbation theory, as inferred by condition (4-5).

As Z increase the structures become more open and linear screening becomes inadequate. Covalent structures have large fluctuations in the potential (25) and perturbation theory fails, even if the valence difference is zero or one. Thus, covalent semiconductor compounds and alloys are in general beyond the scope of first principles, linearly screened, pertur-

bation theory.

Although the expression for $V(\vec{r})$ for a ternary alloy will have more terms than equation (4-3), the number of reciprocal lattice vectors to sum over is the same for a binary or ternary alloy, of a given structure. The total number of matrix elements is the same. Since there are more sums over reciprocal lattice vectors in an expression for $V(\vec{r})$ in a ternary alloy, each sum will have less reciprocal lattice vectors to sum over. Each sum over $\vec{q}$ can also be reduced by the concentration factor, since for a ternary alloy $C_A + C_B + C_C = 1$ where as $C_A + C_B = 1$ for a binary alloy.

The quantities making the sums large or small will still be the averages and differences of atomic form factors evaluated at the important reciprocal lattice vectors. The invalidation of perturbation theory arises from having large fluctuation in the crystal potential. This occurs in a ternary alloy for the same reasons it does in a binary alloy, therefore the same restrictions should hold for both binary and ternary alloys.

CHAPTER 5

CONCLUSION

The expression for the band structure energy was expanded for a ternary alloy in terms of the average and difference of ionic pseudo-potentials, just as in the case of a binary alloy. The expression is general, inasmuch as binary and more restricted structural types of expressions (5) and (10) can be derived from it. The expression, however, was seen to be restricted in two ways. Firstly, the geometry of the structure must be such that all sites in the crystal are equivalent (22), and secondly, the use of perturbation theory and linear screening was seen to result in restrictions on the openness of the structure and the valence difference of the constituent atoms. While the theory still includes a large number of alloys, including most metallic alloys, where the structures are close-packed, the semiconductor, covalent compounds and alloys are seen to be excluded.

Katada et al (18) has modified the pseudopotential theory of binary alloys to include structures with non-equivalent sites, although it is still subject to the breakdown of perturbation theory. Phillips (16) has modified pseudopotential theory to account for covalent or open structures. Possibly some sort of fusion of these two theories would enable pseudopotential theory to be applied to even the complex semiconductors.

APPENDIX A

GENERAL FORM OF $\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle$

On specifying that $\vec{q}$ is a reciprocal lattice vector (3-5) becomes

$$\langle \vec{k}+\vec{g}|V(\vec{r})|k\rangle = \left[\frac{1}{m}\sum_{p,s,t}\sum_{r=1}^{(p)(s)(t)} e^{-i\vec{g}\cdot\delta_{p,s,t}^{(i)}}\right]V_A(g)$$

$$+\left[\frac{N_B^p}{pN}\sum_{r=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(i)}}+\frac{N_B^s}{sN}\sum_{s=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(i)}}+\frac{N_B^t}{tN}\sum_{r=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(i)}}\right](V_B(g)-V_A(g))$$

$$+\left[\frac{N_C^p}{pN}\sum_{r=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(i)}}+\frac{N_C^s}{sN}\sum_{s=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(i)}}+\frac{N_C^t}{tN}\sum_{r=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(i)}}\right](V_C(g)-V_A(g)) \qquad (A-1)$$

Collecting the coefficients of each ionic form factor we see that the coefficients of $V_B(g)$ and $V_C(g)$ are as given in equation (A-1). The coefficients of $V_A(g)$ after expanding the first term in (A-1) is

$$\left[\frac{1}{m}\sum_{r=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(i)}}-\frac{N_B^p}{pN}\sum_{r=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(i)}}-\frac{N_C^p}{pN}\sum_{s=1}^{(p)}e^{-i\vec{g}\cdot\delta_p^{(i)}}+\frac{1}{m}\sum_{r=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(i)}}\right.$$

$$-\frac{N_B^s}{sN}\sum_{s=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(i)}}-\frac{N_C^s}{sN}\sum_{s=1}^{(s)}e^{-i\vec{g}\cdot\delta_s^{(i)}}+\frac{1}{m}\sum_{t=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(i)}} \qquad (A-2)$$

$$\left.-\frac{N_B^t}{tN}\sum_{t=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(i)}}-\frac{N_C^t}{tN}\sum_{t=1}^{(t)}e^{-i\vec{g}\cdot\delta_t^{(i)}}\right]$$

Grouping together the coefficients of the three different sums in (A-2) we have

$$\left[\frac{1}{m} - \frac{N_B^p + N_C^c}{pN}\right]\sum_{\delta=1}^{(p)} e^{-i\vec{g}\cdot\vec{\delta}_p^{(\delta)}} + \left[\frac{1}{m} - \frac{N_B^{s} + N_C^s}{sN}\right]\sum_{\delta=1}^{(s)} e^{-i\vec{g}\cdot\vec{\delta}_s^{(\delta)}}$$

$$+ \left[\frac{1}{m} - \frac{N_B^t + N_C^t}{tN}\right]\sum_{\delta=1}^{(t)} e^{-i\vec{g}\cdot\vec{\delta}_t^{(\delta)}} \tag{A-3}$$

Now $N_B^p + N_C^p$ is the number of B and C atoms on primary sites, this must equal the number of primary sites minus the number of A's on primary sites

$$N_B^p + N_C^p = \left(\frac{p}{m}N - N_A^p\right)$$

The coefficient of $\displaystyle\sum_{\delta=1}^{(p)} e^{-i\vec{g}\cdot\vec{\delta}_p^{(\delta)}}$ in (A-3) is then

$$\frac{1}{m} - \frac{\left(\frac{p}{m}N - N_A^p\right)}{pN} = \frac{1}{m} - \frac{1}{m} + \frac{N_A^p}{pN} = \frac{N_A^p}{pN}$$

In the same manner the coefficients of $\displaystyle\sum_{\delta=1}^{(s)} e^{-i\vec{g}\cdot\vec{\delta}_s^{(\delta)}}$ and $\displaystyle\sum_{\delta=1}^{(t)} e^{-i\vec{g}\cdot\vec{\delta}_t^{(\delta)}}$ in (A-3) are $\dfrac{N_A^s}{sN}$ and $\dfrac{N_A^t}{tN}$ respectively.

1

Substituting into (A-3) the coefficient of $U_A(g)$ in (A-1) becomes

$$\left[\frac{N_A^p}{pN}\sum_{\delta=1}^{(p)} e^{-i\vec{g}\cdot\vec{\delta}_p^{(\delta)}} + \frac{N_A^s}{sN}\sum_{\delta=1}^{(s)} e^{-i\vec{g}\cdot\vec{\delta}_s^{(\delta)}} + \frac{N_A^t}{tN}\sum_{\delta=1}^{(t)} e^{-i\vec{g}\cdot\vec{\delta}_t^{(\delta)}}\right]$$

and the general form of $\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle$ is

$$\langle \vec{k}+\vec{g}|V(r)|\vec{k}\rangle = \left[\frac{N_n^p}{pN} \sum_{\delta=1}^{(p)} e^{-i\vec{g}\cdot\delta_p^{(n)}} + \frac{N_a^s}{sN} \sum_{\delta=1}^{(s)} e^{-i\vec{g}\cdot\zeta_s^{(n)}} + \frac{N_a^t}{tN} \sum_{\delta=1}^{(t)} e^{-i\vec{g}\cdot\zeta_t^{(n)}} \right] U_n(g)$$

$$+ \left[\frac{N_b^p}{pN} \sum_{\delta=1}^{(p)} e^{-i\vec{g}\cdot\delta_p^{(b)}} + \frac{N_b^s}{sN} \sum_{\delta=1}^{(s)} e^{-i\vec{g}\cdot\delta_s^{(b)}} + \frac{N_b^t}{tN} \sum_{\delta=1}^{(t)} e^{-i\vec{g}\cdot\zeta_t^{(b)}} \right] U_b(g)$$

$$+ \left[\frac{N_c^p}{pN} \sum_{\delta=1}^{(p)} e^{-i\vec{g}\cdot\delta_p^{(c)}} + \frac{N_c^s}{sN} \sum_{\delta=1}^{(s)} e^{-i\vec{g}\cdot\zeta_s^{(c)}} + \frac{N_c^t}{tN} \sum_{\delta=1}^{(t)} e^{-i\vec{g}\cdot\delta_t^{(c)}} \right] U_c(g) .$$

APPENDIX B

VARIATIONS IN THE FORM OF $\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle$

Consider equation (3-6) for maximum order at the given concentration

$$\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle = V_A(g)\left[\frac{1}{m}\sum_{\delta=1}^{(p)}e^{-i\vec{g}\cdot\vec{S}_p^{(\delta)}}+\frac{1}{m}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\vec{S}_s^{(\delta)}}-\frac{C_B}{s}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\vec{S}_s^{(\delta)}}\right.$$

$$\left.+\frac{1}{m}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\vec{S}_t^{(\delta)}}-\frac{C_c}{t}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\vec{S}_t^{(\delta)}}\right]+V_B(g)\frac{C_B}{s}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\vec{S}_s^{(\delta)}}+V_c(g)\frac{C_c}{t}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\vec{S}_t^{(\delta)}}$$

$$(B\text{-}1)$$

If (B-1) is to have the form $C_A V_A(g)+C_B V_B(g)+C_c V_c(g)$ for some set of
$\vec{g}=\vec{g}'$ then

$$\sum_{\delta=1}^{(p)}e^{-i\vec{g}'\cdot\vec{S}_p^{(\delta)}}=p\ ,\quad \sum_{\delta=1}^{(s)}e^{-i\vec{g}'\cdot\vec{S}_s^{(\delta)}}=s\ ,\quad \sum_{\delta=1}^{(t)}e^{-i\vec{g}'\cdot\vec{S}_t^{(\delta)}}=t \quad \text{for }\vec{g}=\vec{g}' \quad (B\text{-}2)$$

If (B-1) can also have the form $A(V_B(g)-V_A(g))+B(V_c(g)-V_A(g))$ for
several sets of $\vec{g}$'s then

$$\langle \vec{k}+\vec{g}|V(\vec{r})|\vec{k}\rangle = V_A(g)\left[m^{-1}\sum_{\delta=1}^{(p)}e^{-i\vec{g}\cdot\vec{S}_p^{(\delta)}}+m^{-1}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\vec{S}_s^{(\delta)}}+m^{-1}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\vec{S}_t^{(\delta)}}\right]$$

$$+\frac{C_B}{s}\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\vec{S}_s^{(\delta)}}\left(V_B(g)-V_A(g)\right)+\frac{C_c}{t}\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\vec{S}_t^{(\delta)}}\left(V_c(g)-V_A(g)\right)$$

and the sum must satisfy $\sum_{\delta=1}^{(s)}e^{-i\vec{g}\cdot\vec{S}_s^{(\delta)}}+\sum_{\delta=1}^{(t)}e^{-i\vec{g}\cdot\vec{S}_t^{(\delta)}}=-\sum_{\delta=1}^{(p)}e^{-i\vec{g}\cdot\vec{S}_p^{(\delta)}}$ for some $\vec{g}=\vec{g}'$

$$(B\text{-}3)$$

Since (B-3) can be satisfied in different ways there is in general more than one form of (B-1) of the type $A(\mathcal{V}_{A}(g) - \mathcal{V}_{A}(g)) + B(\mathcal{V}_{c}(g) - \mathcal{V}_{A}(g))$ and correspondingly more than one set of $\vec{g}$'s. A and B are simple functions of composition.

The restrictions (B-2) and (B-3) imply for actual crystal structures that $\sin(\vec{g}\cdot\vec{\delta}) = 0$ for all basis vectors of the unit cell, therefore

$$\vec{q}\cdot\vec{\delta} = m\,\pi \qquad\qquad \text{for all basis vectors and } \vec{g} \text{ (B-4)}$$

The restrictions (B-2), (B-3) and (B-4) restrict the number of basis vectors of a given kind and also the position of sites in the unit cell. These restrictions are fulfilled only by crystals in which all sites are equivalent.

We see that for the case of complete disorder only the form $[c_{A}\mathcal{V}_{A}(g) + c_{B}\mathcal{V}_{B}(g) + c_{c}\mathcal{V}_{c}(g)]$ is non-zero for all sites equivalent.

APPENDIX C

FORM OF $\left|\langle \vec{k}+\vec{q}\,|V(\vec{r})|\vec{k}\rangle\right|^2$.

After multiplying (3-8) by its complex conjugate each term of the product will contain either $\left(V_{\beta}(q)-V_{A}(q)\right)^2$, $\left(V_{c}(q)-V_{A}(q)\right)^2$ or $\left(V_{\beta}(q)-V_{A}(q)\right)\left(V_{c}(q)-V_{A}(q)\right)$.

The coefficients of these three terms will be grouped into seven types. The coefficients within a given type will be of the same form. Each term in the product of (3-8) and its complex conjugate must be averaged over all possible configurations. This amounts to averaging the coefficients of $\left(V_{\beta}(q)-V_{A}(q)\right)^2$, $\left(V_{c}(q)-V_{A}(q)\right)^2$ or $\left(V_{\beta}(q)-V_{A}(q)\right)\left(V_{c}(q)-V_{A}(q)\right)$, whichever appears in the term to be averaged.

1. __Coefficients of the form__ $\displaystyle N^{-2}\sum_{jj'}^{\frac{N_{\ell}^{P}}{P}} e^{-i\vec{q}\cdot(\vec{r}_{j}-\vec{r}_{j'})}$. (C-1)

This is the type of coefficient that arises when a term in (3-8) is multiplied by its own complex conjugate.

$\vec{r}_{j}$ and $\vec{r}_{j'}$ refer to the same set of lattice points in each configuration. In averaging we must let $\vec{r}_{j}$ and $\vec{r}_{j'}$ go over all possible lattice points in the crystal with the number of $\vec{r}_{j}$ and $\vec{r}_{j'}$ in each configuration equal to $\dfrac{N_{\ell}^{P}}{P}$.

When $\vec{r}_{j}=\vec{r}_{j'}$ the exponential is unity. For every configuration there are $\dfrac{N_{\ell}^{P}}{P}$ such terms, then contribution to the sum for each configuration is $\dfrac{N_{\ell}^{P}}{PN^{2}}$, therefore the average for all configurations is $\dfrac{N_{\ell}^{P}}{PN^{2}}$ for $\vec{r}_{j}=\vec{r}_{j'}$

Of the $\int$ distinct configurations $\vec{r}_j$ will contain a site of the kind under consideration (in this case we consider lattice sites that have a B atom on some particular primary site) in just $\dfrac{N_B^p}{\frac{p}{m}N}\int$ configurations.

Of these $\dfrac{N_B^p}{\frac{p}{m}N}\int$ configurations $\vec{r}_j{}'$ will contain one of the remaining

$\left(\dfrac{N_B^p}{p}-1\right)$ sites in $\dfrac{\left(\frac{1}{p}N_B^p-1\right)N_B^p}{\left(\frac{1}{m}N-1\right)\frac{p}{m}N}\int$ configurations.

For this particular $\vec{r}_j$ and $\vec{r}_j{}'$ the averaged contribution to the sum is

$$\frac{1}{N^2}\left[\frac{\left(\frac{1}{p}N_B^p-1\right)N_B^p}{\left(\frac{1}{m}N-1\right)\frac{p}{m}N}\int\right]e^{-i\vec{q}\cdot(\vec{r}_j-\vec{r}_j{}')}$$

divided by the number of configurations.

We now sum up all the averaged contributions for the $\vec{r}_j\neq\vec{r}_j{}'$ when they go over all lattice points.

We do this first by summing over all $\vec{r}_j$ and $\vec{r}_j{}'$ and then subtracting the $\vec{r}_j=\vec{r}_j{}'$

$$\sum_{jj'}^{\frac{N}{m}}\frac{1}{N^2}\left[\frac{\left(\frac{1}{p}N_B^p-1\right)N_B^p}{\left(\frac{1}{m}N-1\right)\frac{p}{m}N}\right]e^{-i\vec{q}\cdot(\vec{r}_j-\vec{r}_j{}')}-\frac{\frac{1}{m}N}{N^2}\left(\frac{\frac{1}{p}N_B^p-1}{\frac{1}{m}N-1}\right)\frac{N_B^p}{\frac{p}{m}N}$$

We let the crystal become large and put $\dfrac{N_B^p}{p}-1=\dfrac{N_B^p}{p}$

and $\dfrac{N}{m}-1=\dfrac{N}{m}$ which means keeping only terms to lowest order in

$\dfrac{p}{N_B^p}$ as in (5 – page 145).

$$\frac{N_B^{p2}}{(\frac{p}{m})^2 N^2} \left[\frac{1}{N^2} \sum_{jj'}^{\frac{N}{m}} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_{j'})} - \frac{1}{mN} \right] \tag{C-2}$$

the sum in (C-2) is zero for $\vec{q} \neq \vec{g}$

Then the averaged contribution from $\vec{r}_j = \vec{r}_{j'}$ in (C-1) is

$$-\frac{N_B^{p2}}{\frac{p^2}{m} N^3}$$

adding to this the contribution for $\vec{r}_j = \vec{r}_{j'}$ we get

$$\frac{N_B^p}{pN^2} - \frac{N_B^{p2}}{\frac{p^2}{m} N^3} = \frac{N_B^p (pN - N_B^p m)}{p^2 N^3} \tag{C-3}$$

All other coefficients of the type 1 will have averaged values in the

same form as (C-3)

2. Coefficients of the form $\underline{N^{-2} \sum_{j}^{\frac{N_B^p}{p}} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_a - \delta_p^{p'})}}$

In this case the $\vec{r}_j$ refer to lattice points or first primary sites that

contain B atoms. The $\vec{r}_a$ refer to lattice points that have a B atom at

$\delta_p^{p'}$ of their unit cell. Since both vectors are refering to B atoms on

primary sites their number is equal because B atoms are assumed to be

distributed uniformly on primary sites.

To sum for $\vec{r}_j = \vec{r}_a$ we must know how many $\vec{r}_j$ are equal to $\vec{r}_a$ or how many

cells in each configuration will have a B atom on the lattice point and

a B_1 atom on $\delta_p^{p'}$ of that unit cell. The number of such cell is equal to

the probability of a B atom on the lattice point times the probability of

a B atom on the point $\delta_p^{p'}$ times the number of cells.

$$\frac{N_B^p}{p N} \times \frac{N_B^p}{p N} \times \frac{N}{m} = \frac{N_B^{p2} m}{p^2 N}$$

The contribution to the sum for each configuration is $\dfrac{N_B^{p2} m \, e^{+i\vec{q}\cdot\vec{\delta}_p^{(p)}}}{p^2 N^3}$

this is / also the averaged contribution for the $\vec{r}_j = \vec{r}_\alpha$

Of the Γ configurations $\vec{r}_j$ will contain a B atom in just

$$\frac{N_B^p}{\frac{p}{m} N} \Gamma$$

configurations.

Of these $\dfrac{N_B^p}{\frac{p}{m} N} \Gamma$ configurations $\vec{r}_\alpha$ will contain a B at $\vec{\delta}_p^{(p)}$ in just

$$\frac{\left(\frac{1}{p} N_B^p - 1\right)}{\left(\frac{1}{m} N - 1\right)} \frac{N_B^p}{\frac{p}{m} N} \Gamma$$
configurations,

therefore the average contribution to the sum for this $\vec{r}_j \neq \vec{r}_\alpha$ is

$$\frac{1}{N^2} \frac{\left(\frac{1}{p} N_B^p - 1\right)}{\left(\frac{1}{m} N - 1\right)} \frac{N_B^p}{\frac{p}{m} N} \frac{\Gamma}{\Gamma} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_\alpha)} e^{+i\vec{q}\cdot\vec{\delta}_p^{(p)}}$$

The averaged contribution to the sum for all $\vec{r}_j \neq \vec{r}_\alpha$ is

$$\sum_{j \neq \alpha}^{\frac{N}{m}} \frac{1}{N^2} \frac{\left(\frac{1}{p} N_B^p - 1\right)}{\left(\frac{1}{m} N - 1\right)} \frac{N_B^p}{\frac{p}{m} N} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_\alpha)} e^{+i\vec{q}\cdot\vec{\delta}_p^{(p)}} - \frac{N}{m N^2} \frac{N_B^p}{\frac{p}{m} N} e^{+i\vec{q}\cdot\vec{\delta}_p^{(p)}}$$

$$= -\frac{N_B^{p2}}{p N^3} e^{+i\vec{q}\cdot\vec{\delta}_p^{(p)}}$$

Adding to this the averaged contribution for $\vec{r}_j = \vec{r}_x$ we get

$$-\frac{N_B^{\,p2}}{\rho N^3}\, m\, e^{+i\vec{g}\cdot S_p^{(p)}} + \frac{N_B^{\,p2}}{\rho N^3}\, m\, e^{+i\vec{g}\cdot \delta_p^{(p)}} = 0$$

Coefficients of this type vanish when they are averaged over all possible configurations.

By comparison with type 2, it is evident that coefficients of the form

$$N^{-2} \sum_{n_j}^{\frac{N_B^{\,p}}{\rho}} e^{-i\vec{g}\cdot(\vec{r}_x + \delta_p^{(a)} - \vec{r}_y - \delta_p^{(p)})} \qquad \text{(type 3)}$$

will also vanish when averaged over all configurations.

4. **Coefficients of the form** $N^{-2} \sum_{j}^{\frac{N_B^{\,p}}{\rho}} \sum_{d}^{\frac{N_C^{\,p}}{\rho}} e^{-i\vec{g}\cdot(\vec{r}_j - \vec{r}_d)}$

These occur in the product of (3-8) and its complex conjugate when the two terms multiplied together are sums both over reciprocal lattice points, but refer to different kinds of atoms. The result is that the two sums have different upper limits. In a given configuration if $\vec{r}_j$ goes to B atoms and $\vec{r}_d$ goes to C atoms, then there is no $\vec{r}_j = \vec{r}_d$ in type 4. Of the Γ configurations $\vec{r}_j$ will contain a B atom in just $\frac{N_B^{\,p}}{\frac{p}{m}N}\Gamma$ configurations.

Of these $\frac{N_B^{\,p}}{\frac{p}{m}N}\Gamma$ configurations $\vec{r}_d$ will contain a C atom in $\frac{N_B^{\,p}}{\frac{p}{m}N}\Gamma \times \frac{N_C^{\,p}}{\frac{p}{m}N}$ configurations.

For this $\vec{r}_j$ and $\vec{r}_d$ the averaged contribution to the sum in type 4 is

$$\frac{1}{N^2} \frac{N_B^p m}{p N} \frac{N_c^p m}{p N} \sum_{\Gamma} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_d)}$$

We now sum up all the averaged contributions for the $\vec{r}_j$ and $\vec{r}_d$ when they go over all lattice points.

$$\sum_{jd}^{\frac{N}{m}} \frac{1}{N^2} \left[\frac{N_B^p m}{p N} \frac{N_c^p m}{p N} \right] e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_d)} - \frac{N}{m N^2} \left[\frac{N_B^p m}{p^2 N^2} N_c^p m \right]$$

$$= \frac{N_B^p N_c^p m^2}{p^2 N^2} \left[\frac{1}{N^2} \sum_{jd}^{\frac{N}{m}} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_d)} - \frac{1}{m N} \right], \qquad \text{(C-4)}$$

the sum in (C-4) is zero for $\vec{q} \neq \vec{g}$

Therefore the averaged value of type 4 is

$$- \frac{N_B^p N_c^p m}{p^2 N^3} \qquad\qquad \text{(C-5)}$$

Other coefficients of this form (type 4) have averaged values of the same form as (C-5).

Coefficients of the form $N^{-2} \sum_{x}^{\frac{N_B^p}{p}} \sum_{y}^{\frac{N_c^p}{p}} e^{-i\vec{q}\cdot(\vec{r}_x + \delta_p^{(2)} - \vec{r}_y - \delta_p^{(2)})}$

$$\text{(type 5)}$$

will also have averaged values of the form $\frac{N_B^p N_c^p m}{p^2 N^3}$

6. __Coefficients of the form__ $N^{-2} \sum\limits_{j}^{N_\beta^P} \sum\limits_{\ell}^{N_\beta^S} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_\ell - \delta_s^{(1)})}$

These occur in the product when a sum over B atoms on lattice sites is multiplied by a sum over B atoms on some site within the cell (in this case the first secondary site)

There will be some $\vec{r}_j = \vec{r}_\ell$ because both refer to lattice points and the same cell could have a B atom on its lattice point and also on its first secondary site inside the cell.

The number of $\vec{r}_j = \vec{r}_\ell$ is the number of such cells $\dfrac{N_\beta^P}{P\frac{N}{m}} \times \dfrac{N_\beta^S}{S\frac{N}{m}} \times \dfrac{N}{m} = \dfrac{N_\beta^P N_\beta^S m}{p\,s\,N}$

Contribution to the sum for $\vec{r}_j = \vec{r}_\ell$ is $\dfrac{N_\beta^P N_\beta^S m}{p\,s\,N^3} e^{-i\vec{q}\cdot\delta_s^{(1)}}$

Of the Γ configurations $\vec{r}_j$ will contain a B atom in $\dfrac{N_\beta^P \Gamma}{\frac{P}{m}N}$ configurations.

Of the $\dfrac{N_\beta^P \Gamma}{\frac{P}{m}N}$ configurations $\vec{r}_\ell$ will have a B atom on $\delta_s^{(1)}$ in just

$$\dfrac{N_\beta^P}{\frac{P}{m}N}\,\Gamma\,\dfrac{N_\beta^S}{\frac{S}{m}N} \qquad \text{configurations.}$$

The averaged contribution to the sum is then

$$\dfrac{1}{N^2}\left[\dfrac{N_\beta^P}{\frac{P}{m}N}\,\dfrac{N_\beta^S}{\frac{S}{m}N}\right] e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_\ell)} e^{-i\vec{q}\cdot\delta_s^{(1)}}$$

The sum of all averaged contributions when $\vec{r}_j$ and $\vec{r}_\ell$ go over the whole lattice and $\vec{r}_j \neq \vec{r}_\ell$ is

$$\sum_{j\ell}^{\frac{N}{m}} \frac{1}{N^2} \left[\frac{N_\theta^P}{\frac{P}{m}N} \frac{N_\theta^S}{\frac{S}{m}N} \right] e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_\ell)} e^{-i\vec{q}\cdot\delta_s^{(1)}} - \frac{1}{mN} \frac{N_\theta^P}{\frac{P}{m}N} \frac{N_\theta^S}{\frac{1}{m}N} e^{-i\vec{q}\cdot\delta_s^{(1)}}$$

$$= \frac{N_\theta^P N_\theta^S m^2}{p\,s\,N^2} \left[\frac{1}{N^2} \sum_{j\ell}^{\frac{N}{m}} e^{-i\vec{q}\cdot(\vec{r}_j - \vec{r}_\ell)} - \frac{1}{mN} \right] e^{-i\vec{q}\cdot\delta_s^{(1)}} \qquad\qquad \text{(C-6)}$$

$$= - \frac{N_\theta^P N_\theta^S m}{p\,s\,N^3} e^{-i\vec{q}\cdot\delta_s^{(1)}}$$

because the sum in (C-6) is zero for the $\vec{q} \neq \vec{g}$

When we add the contribution for $\vec{r}_j = \vec{r}_\ell$ and $\vec{r}_j \neq \vec{r}_\ell$ for the averaged sum of type 6 we see that it vanishes.

Therefore coefficients of the type 6 when averaged over all configurations are zero.

Coefficients of the form $\dfrac{1}{N^2} \sum_{p}^{\frac{N_\theta^P}{\rho}} \sum_{d}^{\frac{N_\theta^S}{\sigma}} e^{-i\vec{q}\cdot(r_p + \delta_p^{(2)} - r_d - \delta_s^{(1)})}$

will also average to zero as does type 6 because we see that some $\vec{r}_p$ and $\vec{r}_d$ are equal.

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