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# On the Causes of Compositional Order in the $\mathrm{Ni}_c\mathrm{Pt}_{(1-c)}$ Alloys

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B.L. Györffy[1]   F.J. Pinski[*][2]   B. Ginatempo[†][3]   D.D. Johnson[‡][4]
J. B. Staunton[§][5]   W. A. Shelton[¶][6]   D. M. Nicholson[‖][6]
G.M. Stocks[**][6]

[1] H.H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, U.K.

[2] Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

[3] Istituto di Fisicai Teorica, Universta di Messina, Messina, Italy.

[4] Sandia National Laboratories, Livermore, California 94551-0969, U.S.A.

[5] Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

[6] Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, U.S.A.

### Abstract

We review, briefly, the arguments which gave rise to the current controversy concerning the origin of compositional order in $\mathrm{Ni}_c\mathrm{Pt}_{(1-c)}$ alloys. We note that strain fluctuations play an important role in determining the state of compositional order in this system and outline a theoretical framework that takes account of them.

## 1 The Nature of the Dilemma

As shown in fig.1 at high temperatures ($T > 1000$ K) $\mathrm{Ni}_c\mathrm{Pt}_{(1-c)}$ alloys form FCC solid solutions for all concentrations [1]. Moreover, they display a robust tendency for compositional order. Experimentally this manifests itself in significant ordering type short range order in the disordered, solid solution phase and in formation of various ordered structures ($L1_2$, $L1_0$ etc.) upon slow cooling to low temperatures. The former is observed in neutron diffuse-scattering experiments [2] and the evidence for the latter is provided

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[§] Work partially supported by Science and Engineering Research Council, U.K. and NATO

[¶] Present address: Computational Physics Inc., P.O. Box 788, Annandale, Virginia, U.S.A.

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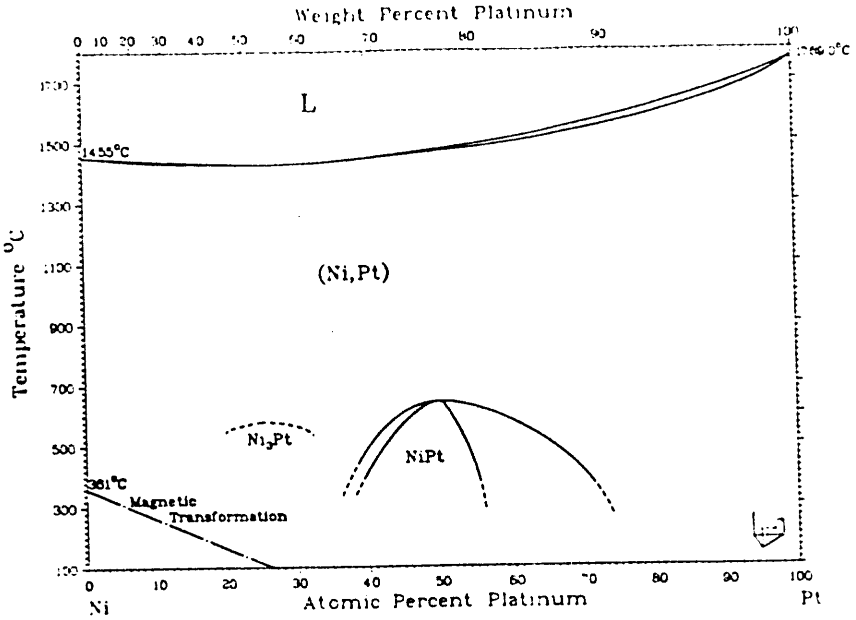

Figure 1: NiPt phase diagram [1]

by the well studied super-lattice Bragg peaks. Concentration oscillations at the surfaces of these alloys [3] also suggest a strong thermodynamic preference for Ni-Pt rather than Pt-Pt or Ni-Ni neighbours. Phonons, measured and calculated also tell the same tale [4]. The dilemma we shall discuss here concerns not the fact but the physical origin of the above well established phenomena.

There are two microscopic approaches to the problem of explaining the occurrence of compositional short and long range order. The first is based on effective lattice Hamiltonians which describe the system in terms of the occupational variable $\xi_i$ which takes the value 1 if there is an A atom at the $i$-th site and 0 if the atom at the $i$-th site is of the B type, and semi-phenomenological interaction parameters. For pairwise interactions only, such a Hamiltonian takes the form

$$H = \frac{1}{2}\sum_{ij}[v_{ij}^{AA}\xi_i\xi_j + v_{ij}^{AB}\xi_i(1-\xi_j) + v_{ij}^{BA}(1-\xi_i)\xi_j + v_{ij}^{BB}(1-\xi_i)(1-\xi_j)] \qquad (1)$$

where $v_{ij}^{\alpha\beta}$ is the interaction energy between an $\alpha$ (=A or B) and a $\beta$ (=A or B) type atom at the sites $i$ and $j$ respectively. In this language an ordering tendency is due to AB bonds being more attractive than AA or BB bonds, namely, $v_{ij} \equiv v_{ij}^{AA} + v_{ij}^{BB} - 2v_{ij}^{AB} > 0$ By contrast $v_{ij} < 0$ implies clustering. If the parameters are not known apriori but are determined by fitting to experimental data, (which is the usual modus operandii when applying this approach [5],[6]) no conflict arises between theory and experiments as to the cause of ordering. Indeed, Dahmani et al.[2] found, by fitting to the results of their neutron scattering experiments in the $Ni_cPt_{(1-c)}$ alloys, that $v_{ij}$ is large and positive for nearest neighbour sites and very small for $i$ and $j$ further apart. So at this level of description there is, again, no controversy. However, the matter becomes more complicated if we follow the alternative approach and attempt to answer the question of what drives the ordering process on the basis of a, more or less, first principles, electronic, description of the concentration fluctuations. It is at this level that the observed behaviour of the $Ni_cPt_{(1-c)}$ system becomes problematic.

In short, fairly general, theoretical arguments suggest that alloys of transition metals with roughly half filled d-bands order while those with almost full or almost empty d-bands cluster in the disordered state and, therefore, phase separate at low temperatures [7], [8], [9],[10], [11]. Moreover, this prediction is borne out by a considerable body of experimental data [10], [11]. However, there are many exceptions to the above *rule*. Of these $Ni_cPt_{(1-c)}$ is one of the best known examples [12].

Treglia and Ducastelle [12] studied this case with some care. However, using an otherwise fairly reliable theoretical scheme, based on a tight-binding model Hamiltonian for describing the electrons, they concluded that there was no simple way of avoiding the prediction that $Ni_cPt_{(1-c)}$ should cluster in the disordered phase and phase separate at low temperatures. In the end, they suggested that the spin-orbit coupling, which was neglected in their non-relativistic treatment of the problem, might give rise to a repulsion between the Pt atoms and hence override the usual band filling argument. To substantiate or reject this interesting hypothesis was the purpose of two recent reconsiderations of the problem by Pinski et al. [13] and Lu et al. [14], [15]. Unfortunately, these calculations resulted in apparently conflicting results. The first suggested that the ordering tendency in the $Ni_cPt_{(1-c)}$ system is due to a size effect overriding the band filling mechanism whilst Lu et al. [14] concluded that it is a relativistic effect but not specifically to do with the spin-orbit coupling. In this note we wish to examine the implications of these seemingly conflicting results.

The calculations themselves are quite straightforward in both cases and as such are not contoversial. Pinski et al. [13] calculated the Warren-Cowley short-ranged order parameter $\alpha(q)$ and found that it increases from the centre of the Brillouin zone ($\Gamma$-point) to the zone boundary (X-point) indicating an ordering tendency (see fig.2). In addition

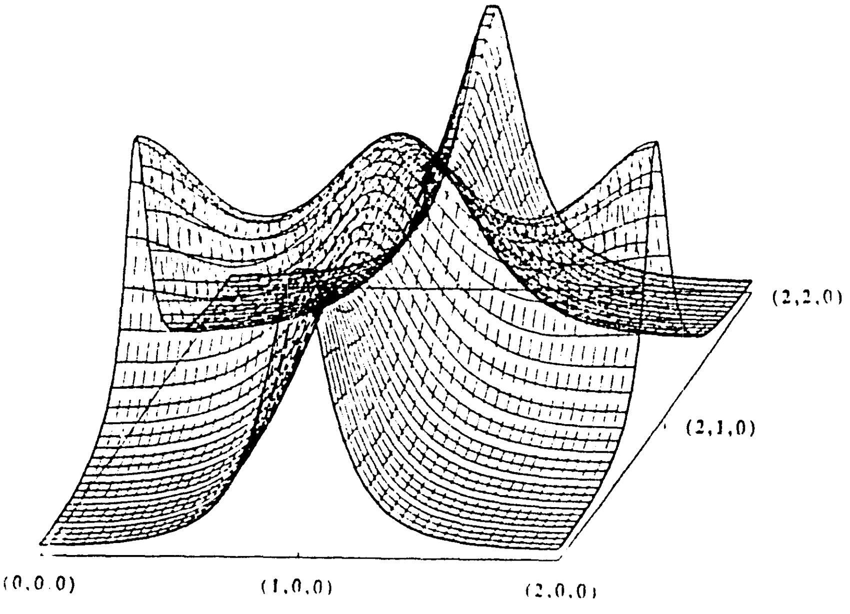

Figure 2: $\alpha(\vec{q})$in the $q_z = 0$ plane for $Ni_{0.5}Pt_{0.5}$ for a temperature about 10% greater than the theoretical ordering temperature. The peaks are at the X-points of the FCC Brillouin zone, indicating the tendency for the alloy to order along the (100) direction, i.e. into the $L1_0$ structure at low temperatures [13]

to self-consistency, these calculations differed from those of Treglia and Ducastelle [12] in their treatment of what, in tight binding language is called *off diagonal* randomness. It was then argued that this feature, which is the consequence of the size difference between the Ni and Pt atoms, was responsible for suppressing the normally powerful band filling mechanism. On the other hand, Lu et al. [14], [15] calculated the formation enthalpy

$$\Delta E(V_{L1_0}, V_{Ni}, V_{Pt}) = E(NiPt, V_{L1_0}) - \frac{1}{2}[E(Ni, V_{Ni}) + E(Pt, V_{Pt})] \qquad (2)$$

where $V_\alpha$ is the equilibrium volume of the system indicated by the suffix $\alpha = L1_0$, Ni and Pt respectively. The calculations were performed using state-of-the-art self-consistent, scalar-relativistic and non-relativistic LAPW calculations [14], [15]. As shown in fig.3 they found that non-relativistically $\Delta E$ is positive implying phase separation at low temperatures, but scalar-relativistically it is negative and, therefore, consistent with the observed ordering tendency. Thus, they concluded that ordering, in these alloys, is a relativistic

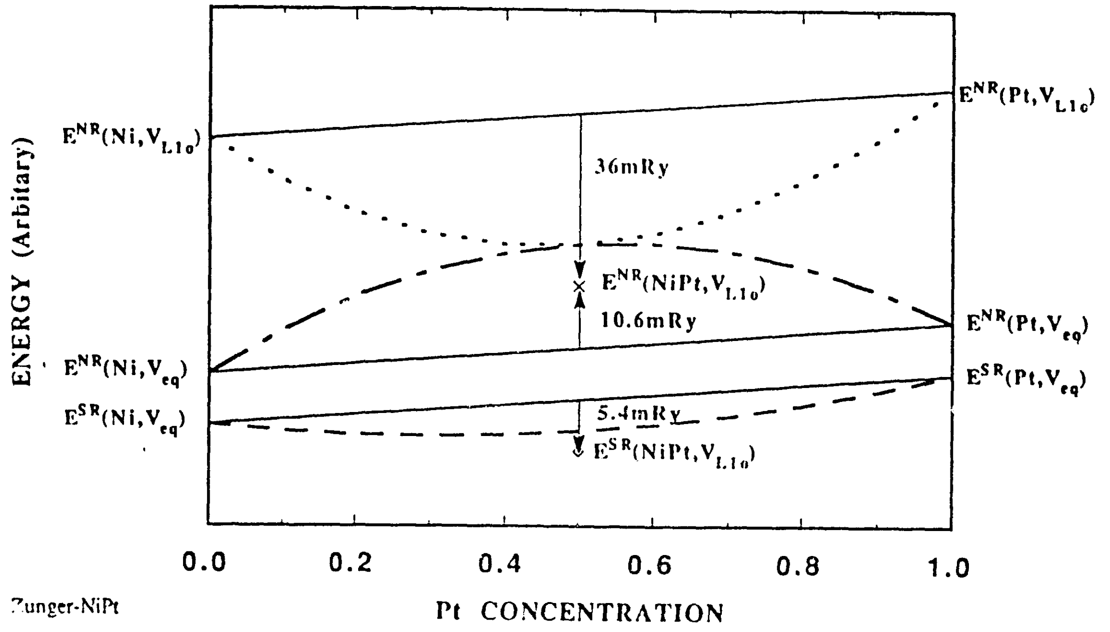

Figure 3: The local density approximation (LDA) ground state energies and configurationally averaged energies of various ordered and disordered NiPt alloys. The superscripts NR and SR denote non-relativistic and scalar-relativistic respectivly. $V_{eq}$ denotes the equilibrium volume for the system specified. $V_{L1_0}$ is the volume of the $L1_0$ ordered compound and $V_{Ni_{0.5}Pt_{0.5}}$ is that for the corresponding solid solution. The points marked by × and ◇ are due to Lu et al. [14] [15]. The dotted line, dot-dashed line and dashed line are the *conjectured* configurationally averaged energies for solid solution alloys as a function of the Ni concentration $c$. The dotted line is for a rigid lattice having the volume of corresponding to the 50/50 alloy. Whilst, the dot-dashed and dashed lines denote non-relativistic and scalar-relativistic calculations performed at the equilibrium volumes of the alloys in question.

effect, albeit they found the mass-velocity and Darwin corrections to be the decisive factor rather than the spin orbit coupling mechanism suggested by Treglia and Ducastelle [12]. In fact they argue that spin-orbit coupling favours clustering.

Before attempting to reconcile the apparently conflicting views we wish to digress briefly in order to discuss the theories of compositional order relevant to the above controversy.

## 2 First Principles Theories of Compositional Order

Currently three ways of proceeding are being actively persued: the first is the effective Hamiltonian approach advocated by Connolly and Williams [17], the second is the electronically based mean field theories of Ducastelle and Gautier [18] and Gyorffy and Stocks [19], [20] and the third is the hybrid, quasi-random structures scheme of Zunger et al. [21]. As the latter has not, as yet, been brought to bear on the problem of ordering in metallic alloys we shall not consider it here any further.

The first strategy consists of determining the energy parameters in lattice Hamiltonians, like the one in eq.1, by requiring that they reproduce the results of first principles total energy calculations for various ordered configurations. The effective Hamiltonian so obtained is then used in full lattice statistical mechanics calculations based on either cluster variational (CVM) or Monte Carlo methods. Clearly, the virtues of this procedure are conceptual simplicity and generality. Its principle draw-back is its lack of foundation in theoretical physics. Namely, there is no guarantee that a suitable lattice Hamiltonian exists which reproduces the complex, non- local, long-ranged energetics of the electron *glue* which holds solids together. For a discussion of the non-covergence of the many-atom-interaction series in solids the reader is referred to the recent paper by Heine et al. [22]. Nevertheless, it often works, although in what follows, its applicability to the $\mathrm{Ni}_c\mathrm{Pt}_{(1-c)}$ case will be the subject of some reservations.

The alternative, mean-field theory, approach does not eliminate the electronic variables to produce a lattice model Hamiltonian but attempts to carry out the required sums over the compositional ensemble in terms of electronic free energies. Of course, this cannot be done without serious approximations. In fact, the only tractable scheme, at the moment, is the mean field theory based on the Coherent Potential Approximation (CPA) treatment of the electrons in the compositionally disordered crystal potential. As a simplification the electrons may be described by a tight- binding model [11], [12], [18] but frequently a fully first-principles multiple scattering method, based on a density functional theory description of the crystal potential, is used [19], [20] (SCF-KKR-CPA).

Clearly, the main shortcoming of the latter approach is the limitation imposed on it by the mean-field theory assumption. On the other hand, it is a very generally applicable procedure since it makes no assumption about the functional form of the variation of the free energy from configuration to configuration. In other words, the free energy is not broken down into $2,3,ldots,n-$body contributions [22]. In particular, the above mean field theory deals readily with the cases where the interactions are long ranged and oscillatory [19], [20]. Furthermore, unlike the Connolly-Williams method, but like the method of quasi-random structures, it deals directly with the disordered state whose instability frequently signals the onset of compositional order. Thus, near the transition temperature, $T_c$, it can be regarded as a first principles Landau theory [6] [20].

Let us now focus attention on the correlation function $\alpha(ij)$ defined by

$$c_i(1-c_j)\alpha_{ij} = \langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle \tag{3}$$

In the disordered state where $c_i = \bar{c}$ for all $i$ and $\alpha(ij)$ depends only on the vector $\vec{\mathbf{R}}_{ij}$ which connects the sites $i$ and $j$, the lattice Fourier transform of $\alpha(ij)$ can be written in terms of the Ornstein-Zernike direct correlation function $\alpha(\vec{\mathbf{q}})$ as follows [19]

$$\alpha(\vec{\mathbf{q}}) = \frac{1}{1-\beta\bar{c}(1-\bar{c})S^{(2)}(\vec{\mathbf{q}})} \tag{4}$$

where $\beta$ is the inverse temperature $1/k_BT$. Note that $\alpha(\vec{\mathbf{q}})$ is the Warren Cowley short-range order parameter mentioned earlier and is measured in diffuse scattering experiments.

The above formula is exact and can be taken as the definition of the direct correlation function $S^{(2)}(\vec{\mathbf{q}})$. The reason for an interest in $S^{(2)}(\vec{\mathbf{q}})$ is that it is more directly related to the interactions between atoms than is $\alpha_{ij}$ which, like the radial distribution function in liquids, is dominated by simple packing considerations. Thus a useful way of comparing different theories and experiments is to compare the direct correlation functions they imply. For instance, the usual mean field approximation [6], [23], [24] for the model Hamiltonian given in eq.1, results in $S^{(2)}(\vec{\mathbf{q}}) = v(\vec{\mathbf{q}})$ which is the lattice Fourier transform of $v_{ij}$. Of course, when the CVM or Monte Carlo calculations are used the relationship between the potential parameters, $v(\vec{\mathbf{q}})$, and the direct correlation function is more complicated. Nevertheless, its calculation in either case is straightforward.

In the case of the first principles mean field theory we have referred to above, $S^{(2)}(\vec{\mathbf{q}})$ works out to be the lattice Fourier transform of

$$S^{(2)}_{ij} = \left( \frac{\partial^2 \Omega^{CPA}}{\partial c_i \partial c_j} \right)_{c_i, c_j = \bar{c}\ \forall i} \tag{5}$$

where $\Omega^{CPA}(\{c_i\})$ is the electronic grand potential averaged, using the coherent potential approximation, with respect to the inhomogeneous product distribution function

$$P(\{\xi_i\}) = \prod_i p_i(\xi_i) \tag{6}$$

with each factor being parameterized by the local concentration $c_i$ as follows

$$p_i(\xi_i) = c_i \xi_i + (1 - c_i)(1 - \xi_i). \tag{7}$$

Starting with the basic equation of the inhomogeneous KKR-CPA, which corresponds to the distribution in eq.6, one can derive an explicit expression for $S^{(2)}(\vec{\mathbf{q}})$ in terms of quantities which are readily available at the end of an SCF-KKR-CPA calculation. From the electronic grand potential, neglecting double counting corrections, an expression for $S^{(2)}(\vec{\mathbf{q}})$ is derived that has the form of a susceptibility. Schematically, it can be written as

$$S^{(2)}(\vec{\mathbf{q}}) = |M|^2 \sum_{\vec{\mathbf{k}}} \int d\epsilon \int d\epsilon' \frac{f(\epsilon) - f(\epsilon')}{\epsilon - \epsilon'} A^B(\vec{\mathbf{k}}, \epsilon) A^B(\vec{\mathbf{k}} + \vec{\mathbf{q}}; \epsilon') \tag{8}$$

where $|M|^2$ indicates matrix elements, $f(\epsilon)$ is the usual Fermi function and $A^B(\vec{\mathbf{k}}, \epsilon)$ is the Bloch spectral function which describes the electronic structure of the random alloy.

As is well known if, in the solid solutiuon, the compositional fluctuations are such that like atoms cluster together $\alpha(\vec{\mathbf{q}})$ has a peak at $\vec{\mathbf{q}} = 0$. In the opposite case of ordering type fluctuations $\alpha(\vec{\mathbf{q}})$ peaks at $\vec{\mathbf{q}}_0 \neq 0$ where $\vec{\mathbf{q}}_0$ is the wave vector of the compositional modulation. In the case of the fluctuations that are precursors to the $L1_0$ ordered state $\vec{\mathbf{q}}_0$ is one of the X-points in the Brillouin zone. It will be of interest later that, in principle, $\alpha(\vec{\mathbf{q}})$ may peak at both the $\Gamma-$ and X-points. This is a very interesting circumstance because it may give rise to competition between phase separation and ordering. In particular, for $c = 0.5$ on a fcc lattice, both phase separation and ordering into the $L1_0$ structure are second order phase transitions and hence are due to instabilities of the disordered phase to $\vec{\mathbf{q}} = 0$ and $\vec{\mathbf{q}} = \vec{\mathbf{q}}_0$ fuctuations respectively. These instabilities are signalled by the divergence of $\alpha(\vec{\mathbf{q}})$ at the appropriate wave vectors. In the case of the two peaks envisioned above, as the temperature is lowered, one of them must win, namely diverge first at the transition temperature $T_c$. The state corresponding to the other may then become a metastable state for $T < T_c$.

Returning to our main concern, we note that the $\vec{\mathbf{q}}$ dependence of $\alpha(\vec{\mathbf{q}})$ for $Ni_{0.5}Pt_{0.5}$ that is shown in fig.2 [13] implies ordering type short range order in the disordered state.

Pinski et al. [13] found that the structure in $\alpha(\vec{\mathbf{q}})$ arose predominantly from hybridization of $t_{2g}$ $d$-states produced by a balance between diagonal and off-diagonal disorder. Namely, the random overlap of atoms drives ordering and overpowers the usual band-filling effect which, for $\mathrm{Ni}_c\mathrm{Pt}_{(1-c)}$, should result in phase separation. The differences between the charge overlaps of Pt-Pt, Pt-Ni and Ni-Ni nearest neighbour pairs may be described as a consequence of Pt being a big atom and Ni being a small atom. Consequently, the above mechanism of ordering was regarded as the quantum mechanical description of the empirical rule, refered to by Hume-Rothery [25], that big atoms and small atoms order if they mix at all.

Whilst these results are in good qualitative agreement with the experimental facts they are, clearly, in conflict with the unexceptionable non-relativistic calculations of Lu et al. [14] which, as will be recalled, yield a positive enthalpy of mixing, $\Delta E$, and hence imply, on the basis of the third law of thermodynamics, phase separation. Although, relativistically they find $\Delta E < 0$ and, hence, conclude that ordering is a relativistic effect the matter needs further attention for two reasons. Firstly, the inconsistency of the non-relativistic results may hid some conceptual flaw in our understanding of ordering and phase separation in alloys. Secondly, whilst the relativistic calculations conclusively indentified the ground state they do not conclusively indentify the ordering mechanism. Fortunately, some recent calculations [15] [16] clarify, to some extent, both aspects of the problem.

Recently, Lu et al. [15] found that, if the ground state energies of the pure metals in eq.2 are calculated at the volume of the ordered $\mathrm{L1_0}$ intermetallic compound, rather than at their respective equilibrium volumes, $\Delta E$ turns out to be negative even in a non-relativistic calculation. Thus as shown in fig.3 $E(L1_0)$ is above the $cE^{NR}(Ni, V_{NiPt}) + (1-c)E^{NR}(Pt, V_{NiPt})$ line because pure Ni contracts and pure Pt expands, compared with the volume of the intermetallic compound, in order to minimize their ground state energy.

Also, we have calculated $\bar{E}(Ni_{0.5}Pt_{0.5}, V_{Ni_{0.5}Pt_{0.5}})$, the configurationally averaged energy for the disordered $\mathrm{Ni_{0.5}Pt_{0.5}}$ alloy, using the same SCF-KKR-CPA method that was used in calculating $\alpha(\vec{\mathbf{q}})$ in our previous paper [13]. As expected, on the basis of the strong ordering tendency we found earlier, $\bar{E}(Ni_{0.5}Pt_{0.5}, V_{Ni_{0.5}Pt_{0.5}})$ lies above $E(NiPt, V_{L1_0})$ [16]. The SCF-KKR-CPA is exact in the impurity limit, for a fixed crystal potential function which, in the present case, is the local density approximation (LDA) functional [20], and therefore reduces, smoothly, to the pure metal calculation for $c = 0$ and 1. Therefore, on the bsis of the above results we conjecture that when the average energy, $\bar{E}(c)$, is calculated as a function of the concentration it will be given by either the dotted or the dot-dashed lines of fig.3 depending on whether the lattice parameter is kept at its value for the $\mathrm{L1_0}$ alloy or is allowed to relax in order to minimise the average energy at each concentration. These conjectures together with fig.2 provide the following simple explanation of the inconsistancy in the non-relativistic theory.

As noted before phase separation is a $\vec{\mathbf{q}} = 0$ instability described by

$$\alpha(0) = \frac{1}{1 - \beta\bar{c}(1-\bar{c})S^{(2)}(0)} \tag{9}$$

where

$$\begin{aligned} S^{(2)}(0) &= \frac{1}{N}\sum_{ij} S^{(2)}_{ij} \\ &= \frac{1}{N}\sum_{ij}\left(\frac{\partial^2\Omega^{CPA}}{\partial c_i \partial c_j}\right) \end{aligned}$$

$$= \frac{1}{N}\frac{\partial^2\Omega^{CPA}(c)}{\partial c^2} \tag{10}$$

and $\Omega^{CPA}(c)$ is the configurationally averaged electronic grand potential for the homogeneous alloy as calculated within the SCF-KKR-CPA. Evidently, $\Omega^{CPA}(c)$ should be used for $E(Ni_cPt_{(1-c)}, V_a)$ in fig.3. Thus, on a rigid lattice $\Omega^{CPA}(c)$ is given by the dotted line in fig.3 and hence $S^{(2)}(0) > 0$ on account of eq.10. Consequently, as is clear from eq.9, $\alpha(0)$ will not diverge at any temperature. This is consistent with the $\alpha(\vec{\mathbf{q}})$ calculated by Pinski et al. [13] non-relativistically and on a rigid lattice. As shown in fig.2 $\alpha(\vec{\mathbf{q}})$ is peaked at the zone boundary and only its value at the X-point can diverge. In short, both the conjectured shape of $\Omega^{CPA}(c)$ on a rigid lattice and the zone boundary value of $\alpha(\vec{\mathbf{q}})$ indicate ordering.

On the other hand if the lattice is allowed to relax at each concentration, $\Omega^{CPA}(c)$ is conjectured to be given by the dot-dashed line in fig.3, thus $\left(\partial^2\Omega^{CPA}(c)/\partial c^2\right) < 0$ and therefore $S^{(2)}(0) > 0$. Consequently, $\alpha(0)$ will diverge at some temperature $T_c^c$ signaling phase separation in agreement with the arguments of Lu et al. [14]. Unfortunately, the function $\Omega^{CPA}(c)$ is not sufficient to determine what will happen to $\alpha(\vec{\mathbf{q}})$ at finite wave vectors. It can only predict that the solid solution will phase separate unless some other instability, at finite $\vec{\mathbf{q}} = \vec{\mathbf{q}}_0$, interfers at some $T_c^o > T_c^c$. Since the mean-field theory used by Pinski et al. [13] was designed to describe compositional fluctuations on a rigid lattice, it is clear that it cannot describe $\alpha(\vec{\mathbf{q}})$ in the present circumstance dominated by lattice relaxation effects.

One way forward is to follow the Connolly-Williams argument [17] and fit effective Hamiltonians to fully relaxed total energy calculations such as those by Lu et al. [14]. Whilst $\alpha(\vec{\mathbf{q}})$ obtained in this way may lead to usefull insights it is frought with difficulties because the potential parameters representing elastic forces are likely to be long ranged.

For these reasons as well as for wishing to describe the ordering process in explicitly electronic terms, in the next section we shall outline a generalization of the mean-field theory that includes an account of stain fluctuations on an equal footing with compositional fluctuations.

## 3 Strain Fluctuations and the State of Compositional Order

Even in crystalline solids atoms do move about. At finite temperature they move from lattice site to lattice site by diffusion, as well as vibrating about their equilibrium positions. In a multicomponent system this means that a given site is occupied by different atoms at different times. Evidently, when a big atom replaces a small one, the environment of the site in question responds by expanding. Alternatively, when a large atom is interchanged with a small atom the neighbouring atoms relax towards the site. Here, we are interested in describing these strain fluctuations whithin the same kind of first principles framework that we applied to concentration fluctuations. Although these strain fluctuations are ubiquitous in metallic alloys and have received considerable experimental and theoretical attention from physicists, metallurgists and material scientists for the best part of a hundred years, very little effort has been directed towards obtaining a fully microscopic, electronic, theory of them. For a careful discussion of this point see Zunger et. al. [26]. Consequently, what follows can only be some very preliminary remarks.

As a straightforward generalization of the mean field theory encapsulated in eqs.3,4,5, 6,7 we may consider the electronic grand potential for the inhomogenous concentration configuration $\{c_i\}$ on a relaxed lattice. That is to say each lattice point $\vec{\mathbf{R}}_i^0$ is assumed to have moved to the relaxed position $\vec{\mathbf{R}}_i = \vec{\mathbf{R}}_i^0 + \vec{\mathbf{u}}_i$ under the influence of the compositional (Kanzaki) forces in order to minimize the free-energy $\Omega^{CPA}(\{c_i\}, \{\vec{\mathbf{u}}_i\})$. Describing the total displacement field by the set $\{\vec{\mathbf{u}}_i\}$, going through the arguments of Gyorffy and Stocks [19] and using the chain rule for differentiating with respect to the local concentrations, we find the following expression for the direct correlation function

$$S^{(2)}_{ij} = S^{c,c}_{ij} + \sum_{l,\alpha} S^{c,u^\alpha_l}_{il} \gamma^\alpha_{lj} \tag{11}$$

where $\alpha = x, y$ and $z$ and

$$S^{c,c}_{ij} = \left( \frac{\partial^2 \bar{\Omega}^{CPA}(\{c_i\}, \{\vec{\mathbf{u}}_i\})}{\partial c_i \partial c_j} \right)_{c_i, c_j = \bar{c}\ \forall i} \tag{12}$$

$$S^{c,u^\alpha_j}_{ij} = \left( \frac{\partial^2 \bar{\Omega}^{CPA}(\{c_i\}, \{\vec{\mathbf{u}}_i\})}{\partial c_i \partial u^\alpha_j} \right)_{c_i, c_j = \bar{c}\ \forall i} \tag{13}$$

$$\gamma^\alpha_{ij} = \left( \frac{\partial u^\alpha_i}{\partial c_i} \right)_{c_i, c_j = \bar{c}\ \forall i} \tag{14}$$

Evidently, the effects of the strain fluctuations on the short range order are described by the new response functions $S^{c,u^\alpha_j}_{ij}$ and $\gamma^\alpha_{ij}$. A theory for the latter, very interesting, quantity (note $\delta u^\alpha_i = \sum_j \gamma^\alpha_{ij} \delta c_j$) can be readily developed in the limit where the displacements, $\{\vec{\mathbf{u}}_i\}$ are regarded as small and their effect on $\Omega^{\mathrm{CPA}}$ is taken into account only in the Harmonic approximation. Under these assumptions we find

$$\gamma^\alpha_{ij} = \sum_{l,\beta} \Phi^{-1}_{\alpha,\beta}(i, l) S^{c,u^\alpha_i}_{li} \tag{15}$$

where the static force constants $\Phi_{\alpha,\beta}(i, j)$ are given by

$$\Phi_{\alpha,\beta}(i, j) = \left( \frac{\partial^2 \bar{\Omega}^{CPA}(\{c_i\}, \{\vec{\mathbf{u}}_i\})}{\partial u^\alpha_i \partial u^\beta_j} \right)_{c_i = \bar{c};\forall i; u^\alpha_i; u^\beta_j = 0;\forall i} \tag{16}$$

The rest of the theory proceeds along lines entirely analogous to that for $S^{c,c}_{ij}$ [19],[20] and the end results are complicated response function formulas (for $S^{c,u^\alpha_j}_{ij}$ and $\Phi_{\alpha,\beta}(i, j)$) which have to be evaluated using the results of a SCF-KKR-CPA calculations for a homogenous solid solution with concentration $\bar{c}$. Although the implementation of the theory is a major computational task, the above formulas provide a fairly concise conceptual framework for contemplating the influence of strain fluctuations on the compositional short ranged order. The extension of these ideas to include long range order is also straightforward.

From the point of view of our present concern there are a couple of simple comments which follow from the above considerations.

I Strain fluctuations induce an elastic contribution to the direct correlation function $S^{(2)}(\vec{\mathbf{q}})$ or, in the mean field theory to the interchange energy $v(\vec{\mathbf{q}})$. As was stressed by Khachaturyan [6], for alloys of large and small atoms this can be a surprisingly large effect and hence it may play an important role in the case of the $\mathrm{Ni}_c\mathrm{Pt}_{(1-c)}$ system.

II Given the way elastic forces propogate in solids the strain fluctuation contribution to $S^{(2)}(\vec{q})$ is bound to be long ranged. Indeed, in the elastic dipole limit, we may expect contributions which fall off as $S_{ij}^{(2)} = |\vec{\mathbf{R}}_{ij}|^{-3}\exp(-\zeta/\vec{\mathbf{R}}_{ij})$. Thus the problem at hand is like that of dislocations where both the short-ranged bonds, in the core, and the long ranged, elastic, forces are equally important. From this point of view, the first principles mean-field theory method advocated here is particularly promising since it requires calculations in $\vec{q}$-space and treats the small and large $\vec{q}$ limits on equal footing. In this respect, it is quite different from supercell or finite cluster based methods [21]. These considerations are also relevant to the applicability of the Connolly-Williams type of approaches. Clearly, to account for large elastic interactions, the effective Hamiltonian must include long-ranged forces for which both the CVM and the Monte Carlo method become difficult to do. Fortunately, as was recently demonstrated by Marias et al. [27], under these circumstances the mean-field theory becomes a better and better approximation.

Having scetched out a framework for treating the effects of strain fluctuations on the ordering process let us return to the dilema posed by the results of the non-relativistic theory. To begin with we note that from eq.11 we have

$$\begin{aligned} S^{(2)}(0) &\equiv \frac{1}{N}\sum_{ij} S_{ij}^{(2)} \\ &= \frac{1}{N}\sum_{ij}\left(S_{ij}^{cc} + \sum_{l,\alpha} S_{il}^{c,u_l^\alpha}\gamma_{i,l}^{\alpha}\right) \\ &= \frac{1}{N}\left(\frac{\partial^2\Omega^{CPA}(c,a)}{\partial c^2} + \frac{\partial^2\Omega^{CPA}(c,a)}{\partial c\partial a}\frac{\partial a}{\partial c}\right) \\ &= \frac{1}{N}\left(\frac{\partial^2\Omega^{CPA}(c,a)}{\partial c^2}\right)_{c=0.5} \end{aligned} \tag{17}$$

Where $a$ is the lattice constant which is assumed to be a function of the concentration $c$. Thus, as anticipated at the end of the previous section, the direct correlation function at the $\Gamma$-point is given by the second derivative of $\Omega^{CPA}(c,a)$, the electonic grand potential for the relaxed lattice. The dot-dashed line in fig.3 is our conjecture for $\Omega^{CPA}(c,a)$. Hence, as before, we conclude that the disordered phase will be unstable to phase separation at $T_c^s$ unless an ordering instability intervens.

Interestingly, such an unusual circumstance has a good chance of occuring in this system. If we assume that the contribution to $S^{(2)}(\vec{q})$ by the strain fluctuations are of the clustering type for all $\vec{q}$ then, by taking the Fourier transform of eq.11 and writing

$$S^{(2)}(\vec{q}) = S^{cc}(\vec{q}) + \sum_{\alpha} S^{c,u^\alpha}(\vec{q})\gamma^{\alpha}(\vec{q}). \tag{18}$$

we arrive at the conclusion that $S^{(2)}(\vec{q})$ is given by a sum of two sets of peaks. The members of one set are centered on the $\Gamma$-points and are the contributions from the second term in eq.18, whilst the second set are located at the X-points and come from the first term. Although possible, it is unlikely that the superposition of such peaks will result in monotonic behaviour of $S^{(2)}(\vec{q})$ and $\alpha(\vec{q})$. In short, along the $\Gamma$-X line we conjecture a two peaked structure for $\alpha(\vec{q})$ in a non-relativistic theory that includes strain fluctuations. Unfortunately, as the temperature is lowered, which of the two gives rise to the first instability will be determined only when full calculations of the new response functions in eq.18 have been calculated.

Nevertheless, it is instructive to analyse the above hypothetical situation a bit further. Of course, at $T = 0$, the absolute free energy minimum is that of the ground state which, given the ground state search of Lu et al. [14], may be safely assumed to be a phase separated state. However, reaching that state from the homogeneous solid solution phase will be difficult if there is a sizable ordering peak, even if it is not larger than the peak at the zone center. The point is that if nearest neighbour exchange of atoms favours unlike neighbour pairs the system will have to wait for long, perhaps astronomically long, times for a small $\vec{q}$ clustering type fluctuation which could ultimately lead to phase separation. Thus a likely outcome of cooling at moderate rates would be a metastable ordered state. Clearly, finding real systems, as opposed to the above hypothetical non-relativistic $Ni_cPt_{1-c}$ alloys, with competing instabilities would be of great physical interest [28].

Finally, let us speculate on the outcome of a relativistic theory that would be directly relavent to the experiments on the $Ni_cPt_{1-c}$ alloy system. The relativistic calculations of Lu et al. [14], displayed in fig.3, suggest that the contribution from strain fluctuations are reduced on account of a relativistic contraction of the Pt atom. Indeed from our conjectured plot of $\Omega^{CPA}(c, a)$ for the relativistic theory shown in fig.3 we expect $\left(\partial\Omega^{CPA}/\partial c^2\right) < 0$ and hence the phase separation instability to be supressed. At the same time we do not expect $S^{c,c}(\vec{q})$ to change very much. In support of this expectation we show in fig.4 the densities of states for the $Ni_{0.5}Pt_{0.5}$ random alloy from non-relativistic

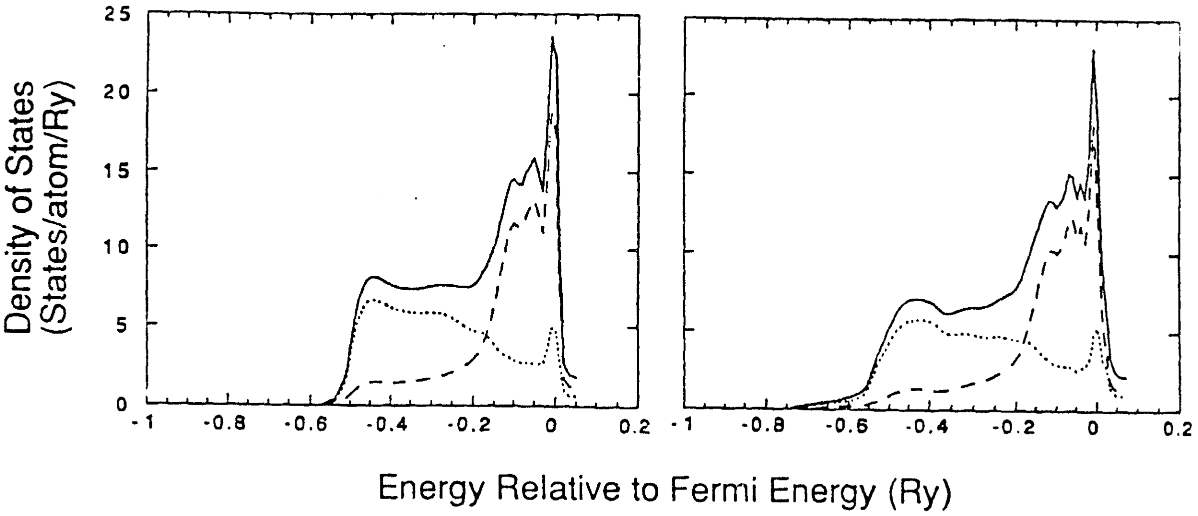

Figure 4: Non relativistic (left) and relativistic (right) SCF-KKR-CPA densities of states (DOS) for $Ni_{0.5}Pt_{0.5}$. Solid line: total DOS. Dashed line: Ni-contribution. Dotted line: Pt-contribution. Charge self consistency reduces the effects of the mass-velocity and Darwin terms, and the relativistic and non relativistic DOS's look surprisingly similar, confirming, indirectly, the validity of the nonrelativistic approach to NiPt.

and fully (Dirac equation [29]) relativistic SCF-KKR-CPA calculations. Suprisingly the differences are small, particularly in the hybridized $d$-band complex which, it will be recalled, is the region in the densities of states identified by Pinski et al. [13] as giving rise to the X-point peak in $\alpha(\vec{q})$. Thus, we may assume that $S^{c,c}(\vec{q})$ obtained on the basis of a fully relativistic theory will have a negative peak at the zone boundary as before. This suggests that $\alpha(\vec{q})$ will have the same shape as in the non-relativistic calculation whose reults are shown in fig.2.

In summary thare are two size effects operating in the proplem: one works through strain fluctuations and leads to reduced solubility, the other is a manifestation of the random overlaps of atoms and can cause ordering even when the band filling argument favours clustering. Evidently, in the context of first principles quantum mechanical calculations the first was discovered by Lu et al. [14] and the second has been identified by Pinski et al. [13]. The cause of order in the $Ni_{0.5}Pt_{0.5}$ alloy may then be described as follows. The relativistic contraction of the Pt s-orbital [14] eliminates the $\vec{q} = 0$ instability and thereby suppresses immiscibility and therefore allows the second size effect to drive the $L1_0$ ordering process. If substantiated by explicit calculations this explanation will fit nicely with Hume-Rothery's general conclusion [25] that:

*"It is therefore natural that, provided the solvent and the solute atoms are of sufficiently similar size to permit the formation of a wide solid solution, the tendency to form superlattices increases with increasing difference in atomic diameters, since the greater this difference, the greater the strain to be relieved. Thus, superlattices are found in the system copper-gold, where the atomic diameters are Cu = 2.54 Å, Au =2.88 Å but not in the system silver-gold, where the sizes of the two atoms are nearly the same."*

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