

Origins of Compositional Order in NiPt Alloys

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We investigate the cause of compositional ordering in fcc Ni_{0.50}Pt_{0.50} on the basis of a first-principles theory of electronic structure and finite-temperature concentration fluctuations. We treat the size effect, electronegativity, and band filling on an equal footing and find that the first of these dominates, leading to $L1_0$ ordering in agreement with experiment. An electronic origin is given for the metallurgical “rule of thumb” that alloys comprised of *big* atoms and *little* atoms tend to order into simple structures.

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In their classic work, Hume-Rothery and Raynor¹ identified, empirically, differences in atomic size, electronegativity, and the electron per atom ratio (e/a), or band filling, as the principle factors which determine compositional and structural order in alloys. Using fairly general arguments based on a tight-binding framework, Heine and Samson² and Bieber and Gautier³ concluded that transition-metal (TM) alloys will order if the Fermi energy ϵ_F falls near half filling of their d band but will cluster (phase separate) if ϵ_F lies near either band edge. Empirically, this is found for alloys within a given TM series, though less so as one progresses from the $3d$ to $5d$ series. For isoelectronic TM alloys, however, there are numerous exceptions³ to this rule, one of the most notable⁴ is the almost-filled d -band system NiPt. Although this alloy system does not form line compounds typical of alloys with near half-filled d bands that are formed from elements within the same TM series, it still strongly orders; its phase diagram being similar to the noble-metal CuAu alloy system. Thus, unlike CuAu, to which tight-binding theory is not relevant since ϵ_F lies above the filled d -band complex, NiPt stands as a glaring exception to band-filling arguments.

In this Letter, we present first-principles, finite-temperature calculations of the Warren-Cowley short-range-order parameters in the disordered state for Ni_{0.5}Pt_{0.5}. Our central result is that, despite a nearly filled d band, Ni_{0.5}Pt_{0.5} shows a (100)-ordering wave commensurate with the $L1_0$ ordered phase observed experimentally. Unlike previous tight-binding calculations,⁴ we include all three Hume-Rothery effects on an equal footing. In this isoelectronic alloy we find that charge transfer, or electronegativity, effects are negligible and play no role in ordering. From a detailed analysis of our calculation, it is clear that the ordering tendency is driven by a balance between, what in the

language of tight-binding model Hamiltonians would be called, diagonal and off-diagonal disorder. In fact, this mechanism is sufficiently strong that it overcomes the clustering tendency favored by the normal band-filling mechanism. Furthermore, off-diagonal randomness is clearly related to a size effect and may be viewed as an electronic manifestation of the metallurgical “rule of thumb” that alloys comprised of *big* atoms and *little* atoms tend to order into simple structures, for example, $L1_0$ on a fcc lattice. Clearly, this is a different picture than that obtained by the tight-binding analysis of Treglia and Ducastelle⁴ in which they found NiPt phase separated unless spin-orbit splitting was included. That our calculations predict the observed ordering lends strong support to the very general, first-principles, mean-field theory of chemical ordering which has been used here. In particular, it highlights the power of the theory to address questions of ordering in circumstances where the three Hume-Rothery factors may be competing.

These calculations are based on the first-principles, mean-field theory of concentration fluctuations of Györfy and Stocks⁵ and the self-consistent, nonrelativistic Korringa-Kohn-Rostoker coherent-potential-approximation (KKR CPA) theory of the energetics and electronic structure of the disordered phase.⁶⁻⁸ The KKR CPA itself is a mean-field theory of the chemical (substitutional) disorder,^{9,10} and is based on a local approximation to density-functional theory.¹¹ It is worthwhile to note that within KKR CPA “off-diagonal” disorder is handled properly by the construction of the local potential on a site. In general, this local potential depends on the occupation of the surrounding sites, and KKR CPA treats this environmental effect in an average way, as is appropriate in a mean-field theory.

The central result of the concentration-wave theory is

that $S^{(2)}(\mathbf{q}, T)$, the lattice Fourier transform of the Ornstein-Zernike direct correlation function

$$S_{ij}^{(2)} = \left[\frac{\partial^2 \Omega^{\text{CPA}}(\{c_i\})}{\partial c_i \partial c_j} \right]_{\forall c_i = c},$$

provides direct information on the stability of the randomly disordered alloy to concentration fluctuations at a given temperature, T . In this equation, Ω^{CPA} is the KKR CPA electronic grand potential for an inhomogeneous configuration specified by the set of site concentrations $\{c_i\}$. The details of the theory and some of its applications are reviewed by Györfy *et al.*¹²

Experimentally, the instability of the disordered phase to ordering may be seen in diffuse electron-, x-ray-, or neutron-scattering measurements. The experimentally measured intensities are directly related to the Warren-Cowley short-range-order parameter $\alpha(\mathbf{q}, T)$ which in turn is related to $S^{(2)}(\mathbf{q}, T)$ through

$$\alpha(\mathbf{q}, T) = c(1-c)[1 - \beta c(1-c)S^{(2)}(\mathbf{q}, T)]^{-1},$$

where $\beta = (k_B T)^{-1}$. The temperature dependence of $\alpha(\mathbf{q}, T)$ arises in two ways: implicitly from the Fermi distribution function in the electronic structure calculations, and explicitly from the entropy of the high- T , chemically disordered state. Note that this formula is very similar to that obtained in pair-potential treatments of short-range order of Krivoglaz,¹³ and of Clapp and Moss.¹⁴ This comparison implies that $S_{ij}^{(2)}$ may be interpreted as a first-principles generalization of the effective, pairwise, chemical-interchange interactions, i.e., $V_{ij} = V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB}$. However, an important distinction is that $S_{ij}^{(2)}$ contains all higher-order interactions and does not depend on a decomposition of the electronic energy into pairwise contributions.

For our present concern, above a critical temperature T_c , the relevant feature of $\alpha(\mathbf{q})$ or $S^{(2)}(\mathbf{q})$ at fixed T is that it either peaks at $\mathbf{q} = 0$ for phase-separating systems or at various high-symmetry points (so-called Lifshitz special points) for ordering systems.¹⁵ Within KKR CPA formalism, structure in $S^{(2)}(\mathbf{q})$ can arise for various reasons. For example, in the CuPd system peaks in $S^{(2)}(\mathbf{q})$ come at (incommensurate) q vectors corresponding to spanning vectors connecting flat sheets of the Fermi surface.^{3,16} For the $\text{Ni}_{0.75}\text{Fe}_{0.25}$ alloy, magnetic and band-filling effects conspire to produce a zone-boundary peak in $S^{(2)}(\mathbf{q})$.¹⁷ In the present paper, we identify a new mechanism which can give rise to peaks at the zone boundary.

In Fig. 1, we plot $\alpha(\mathbf{q})$ at $T = 1700$ K (above our theoretical T_c) in the $q_z = 0$ plane of the extended zone for $\text{Ni}_{0.50}\text{Pt}_{0.50}$. Clearly, $S^{(2)}(\mathbf{q})$ peaks at the X point, i.e., the (100) Lifshitz special point, indicating instability to $L1_0$ ordering. This calculation is based on self-consistent KKR CPA potentials^{5,6} for disordered $\text{Ni}_{0.50}\text{Pt}_{0.50}$, at the experimentally observed lattice spacing. By lattice Fourier transforming $S^{(2)}(\mathbf{q})$, we obtain a real-

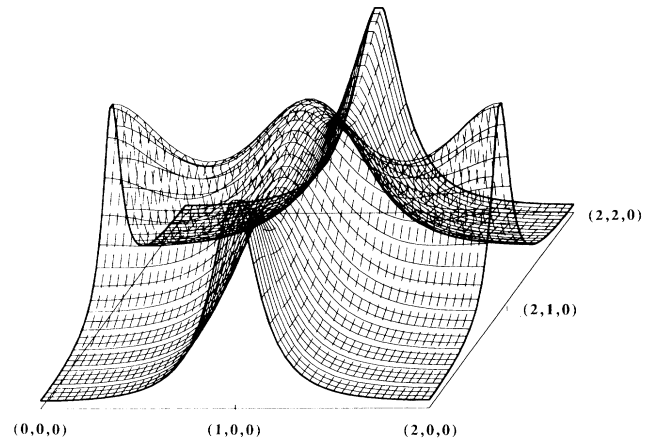


FIG. 1. In the $q_z = 0$ plane, $\alpha(\mathbf{q})$ (in arbitrary units) is displayed for a temperature about 10% greater than the theoretical ordering temperature. The peaks are at the X points of the Brillouin zone, indicating the tendency for the alloy to order along the (100) direction, i.e., the $L1_0$ structure, at low temperatures.

space shell-by-shell representation, $S_n^{(2)}$. These chemical-interchange energies for the first four neighbor shells are -4.7 , -0.4 , -0.2 , and 0.1 mRy, respectively. Clearly, the nearest neighbor $S_n^{(2)}$ dominates which implies a robust ordering, as was deduced from experiment by Dahmani *et al.*¹⁸ We find that the calculated T_c of 1500 K is larger than the observed 890 K. The discrepancy between theory and experiment is much larger than that found in previous calculations for other systems,¹² and is larger than expected from a mean-field theory. Thus, it is likely that a relativistic treatment of the electronic structure is important for determining T_c accurately.

In addition to describing the overall ordering tendency, the calculation also provides detailed information about the electronic origin and nature of this propensity to order. The peak in $\alpha(\mathbf{q})$ at the X point, indicating $L1_0$ ordering, arises from the states at the bottom of the d -band complex. In Fig. 2, we show total and partial densities of states for the random alloy. The Pt states lie predominantly at low energies, while most of the Ni states are just below the Fermi level. However, through hybridization, the important effect of the alloying is to create and to occupy low-lying bonding d states at the expense of the antibonding states around the Fermi level. Notably, these states are well below the d band of elemental Ni. Thus, the ordering tendency seen in $S^{(2)}(\mathbf{q})$ results from occupation of these low-lying, hybridized states which lowers the energy as the number of unlike neighbors increases.

Furthermore, these bonding states have t_{2g} symmetry with lobes pointing towards the nearest neighbors in the fcc structure, ensuring that the peak of $\alpha(\mathbf{q})$ will occur at the X point rather than elsewhere in the zone. The

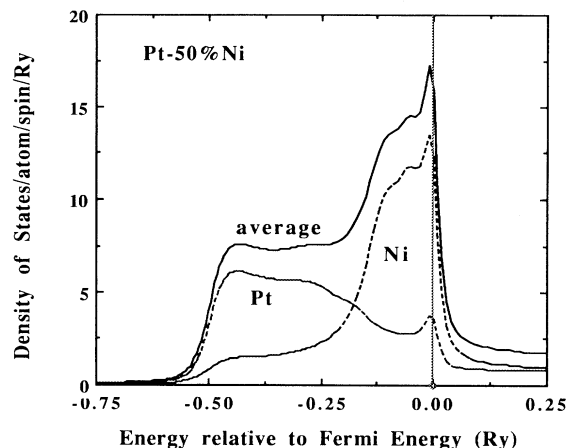


FIG. 2. The density of states $\text{Ni}_{0.50}\text{Pt}_{0.50}$ as a function of energy. The solid line is the average with the dashed lines showing contributions on the Pt and Ni sites.

short-ranged nature of $S_{ij}^{(2)}$ is derived from two sources. First, these bonding states lie over a broad range of energy, necessarily implying that a broad range of momentum contributes to $S^{(2)}$. Second, these states are broadened in momentum due to the disorder; consequently, the corresponding electrons have short coherence lengths. In contrast, standard susceptibility arguments suggest that sharp states in a narrow range of energies near ϵ_F produce the major contributions to the susceptibility. Since the structure in $S^{(2)}(\mathbf{q})$ arises from low-lying states, the ordering will be insensitive to the exact position of the Fermi energy. Thus, changing the e/a ratio in a rigid-band fashion will not alter our conclusions.

We note that the similarity of the electronegativity of Ni and Pt implies that each atom will have to be more or less neutral in the alloy, and hence charge transfer is small. This is what is seen in the calculation. For these isoelectronic species from the end of the TM series, the d states on both kinds of sites will have to be nearly filled and hence the tops of the d bands will be pinned together at ϵ_F . In the tight-binding picture,⁴ this translates into both diagonal and off-diagonal disorder. From our calculations, it is clear that for the effects of off-diagonal disorder to play the important role for ordering a substantial degree of diagonal disorder is necessary. In general, we expect that the balance of diagonal and off-diagonal disorder determines whether a system will order or phase separate, since the position and occupation of the hybridized states are determined by this balance. Clearly, this mechanism is bound to play a more important role in alloys composed of “small” and “big” atoms, as in NiPt.

In a metallurgical picture, this “size effect” (or strain energy) arises from “pressure” associated with close-packing hard spheres of different radii, which, for example, is the basis of the Hume-Rothery 15% (size-effect)

rule¹ in which a solute atom with a radius that is more than $\pm 15\%$ different than the host’s radius will be insoluble. In a quantum-mechanical picture, the electronic structure determines the equilibrium lattice parameter of a system and thus the “sizes” of its constituents. From the discussion above, it is clear that the separation of the d bands (i.e., diagonal disorder) and the difference in d bandwidths (i.e., off-diagonal disorder) of the constituent metals in the TM alloy, and hence the filling of the hybridized d states, gives rise to “electronic pressure” which determines the lattice parameter of the alloy. To elaborate, in the random solid solution, the individual Ni (Pt) site will be expanded (compressed), as compared to the pure metals. Then it follows that ordering which results in each atom being preferentially surrounded by unlike nearest neighbors will be energetically favorable because it reduces the pressure on both kinds of sites, positive in the case of Pt and negative in Ni. Our electronic structure calculations provide an adequate account of the quantum-mechanical manifestations of this size effect. In this context, we point to the work of Mookerjee and Singh¹⁹ which also concluded that the size effect is all important for the lattice dynamics of NiPt alloys. We stress that while s , p , and d states play an important part in determining the lattice constant, or size, the overlap of d bands and the difference in d bandwidths play the key role in producing the hybridization which determines both the chemical ordering and the size effect. For this isoelectronic alloy, the constituent atom with the *bigger* d bandwidth is also the *bigger* atom which connects the microscopic view to the above classical view of size and which, therefore, gives an electronic origin of the metallurgical, big-atom–small-atom ordering tendency.

Given the robustness of this mechanism, we conjecture that the same mechanism is operative in other systems such as the classic order-disorder system CuAu. Indeed, structure in the calculated density of states of Cu_3Au (Ref. 20) is very similar to that which we find in NiPt. Only the placement of ϵ_F is markedly different and, as we have remarked, this mechanism is insensitive to ϵ_F placement. It is also the case that short-ranged interactions of the kind which result from this mechanism produce a good description of the phase diagram of CuAu.²¹ In other isoelectronic Hume-Rothery systems where the d bands do not hybridize due to large diagonal disorder, such as ZnCd, there is a miscibility gap, and no longer should the d bandwidth be correlated with size. The extent to which this mechanism plays a role in other TM systems, and how it depends on the underlying symmetry of the Bravais lattice, has yet to be determined.

We note that Treglia and Ducastelle⁴ obtained ordering in NiPt only by having a spin-orbit split Pt site energy straddling the Ni site band. This, however, requires an unphysically large Pt spin-orbit splitting. Furthermore, one can argue that strong hybridization between light and heavy atoms tends to reduce spin-orbit splitting²² and that mass-velocity shifts in the d band are

effectively canceled through the charge self-consistency process. All this can be verified by comparing relativistic and nonrelativistic linear muffin-tin-orbital (LMTO) calculations for the ordered phase,²³ for example. So why do we find a result different from Treglia and Ducastelle, who found clustering as the dominant concentration fluctuation in the NiPt system when relativistic effects were ignored?

The most obvious difference between our calculation and their tight-binding model is their neglect of the different d bandwidths of Pt and Ni. Indeed, citing Bieber and Gautier,³ they argued that off-diagonal disorder would further accentuate the propensity to phase segregate. This is opposite to our findings, which take proper account of off-diagonal disorder (and charge-transfer effects), unlike the various tight-binding formulations of the CPA.^{24,25}

In summary, we have found that (i) the nonrelativistic self-consistent-field KKR CPA theoretical framework predicts ordering in NiPt alloys without the introduction of *ad hoc* parameters; (ii) the ordering mechanism is critically related to the balance of "diagonal" and "off-diagonal" disorder, which also provides an electronic origin for the ordering in big-atom-little-atom transition-metal systems; and (iii) the effects of relativity are small and can be neglected for the purposes of understanding the origins of ordering in this system, although they may be necessary for obtaining a more accurate prediction of the transition temperature.

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