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LETTER TO THE EDITOR

Fermi surface origin of non-stoichiometric ordering in CuPd alloys

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Abstract

We discuss the peculiarities of the CuPd phase diagram in relation with the Fermi surface of the random alloys, on the basis of first-principle calculations. In particular we study the Fermi surface nesting vectors as functions of the concentration and along a tetragonal Bain path. It turns out that the nesting vectors that can be associated with the experimentally observed ordering transitions towards the $B2$ phase and $L1_2$ phases are commensurate with the lattice only at non-stoichiometric concentrations. The competition between this frustration effect and the electrostatic gain obtained by chemical ordering determines the critical concentrations for the transitions. We argue that the inclusion of these Fermi surface frustration effects is necessary to obtain agreement between theory and experiment on the determination of the phase diagram.

Binary alloys of transition with noble metals display a large variety of low-temperature phases. Interestingly, some of these alloys, although isoelectronic, present different phase diagrams, with apparent exceptions to the empirical *band-filling* Hume–Rothery rule [1]. This is the case (see for example [2]) of $M_{1-c}Cu_c$ alloys, where M stands for one of the metals in the last column of the transition series (namely, Pd or Pt), with the valence electrons per atom ratio, e/a , increasing from 10 to 11 as the Cu atomic content, c , varies from zero to one. All these alloys, in the whole concentration range, present a fcc solid solution phase at high temperature, and their phase diagrams are quite similar in the Cu-rich region, say $c \geq 0.75$; both order into the $L1_2$ lattice, a structure whose prototype is Cu_3Au , i.e. a *geometrical* (i.e. regardless from the site occupation) fcc lattice with AB and A lattice planes alternating along the $[0, 0, 1]$ direction. Interestingly, however, the $L1_2$ stability region lies *above* the stoichiometric molar fraction, $c = 0.75$, and the Cu content corresponding to the highest transition temperature (hereafter referred to as c_{MAX}) is $c_{MAX} \simeq 0.85$, while in a relatively narrow concentration interval, just above $c = 0.75$, only long period superstructures (LPSs) compatible with the $L1_2$ ordering are found [2]. The most surprising facts, however, occur around the equiatomic concentration: CuPt orders into the rhombohedral $L1_1$ structure (of which this alloy is actually

the prototype), a fcc lattice with A and B planes alternating along the [1, 1, 1] direction; while CuPd orders into the B2 structure (CsCl), a bcc lattice with A and B planes alternating along the [0, 0, 1] direction. The fcc–B2 transition in CuPd requires a structural change and chemical ordering to occur simultaneously and is a typical example of a *bainitic* transformation [3]. The occurrence of two different low-temperature phases for these two isoelectronic alloy systems constitutes a striking *violation* of the Hume–Rothery rule on e/a that can be explained in terms of the relevant electronic structures and of the interplay between charge transfers and lattice strains [4, 5]. What has not yet been explained, and constitutes the question we are trying to answer with the present letter, is the experimental evidence that the maximum transition temperature for CuPd corresponds to the *overstoichiometric* value of $c_{MAX} \simeq 0.60$.

Since the 1960s, the Cu-rich region of these phase diagrams have been related to the Fermi surface (FS) shape [6–8], through the so-called FS nesting mechanism. Since the 1980s, the concentration functional theory of Györfy and Stocks [9, 10], a *first-principle* version of the Ginzburg–Landau theory, provided a convenient *quantitative* theoretical framework for describing such phenomena. Its application to many different alloy systems has been successful and it has been generalized to magnetic transitions in connection with the disordered local moments model [11], to the study of the magneto-crystalline anisotropy [12] and to the oscillatory exchange coupling in magnetic multilayers [13].

Very briefly, the concentration functional approach suggests searching for the instabilities with respect to static concentration waves [14],

$$c(\vec{r}) = \sum_{\vec{q}} c_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \quad (1)$$

of the homogeneous, high-temperature, solid-solution phase. The corresponding susceptibility is approximated by the mean-field theory for random alloys, for example the coherent potential approximation (CPA) [15], and is related, via the fluctuation-dissipation theorem, to the Warren–Cowley factor, accessible by diffuse scattering experiments, or to the probability that a concentration fluctuation with a wavevector \vec{q} can occur. At temperature T , the relevant susceptibility is

$$\chi(\vec{q}, T) \propto \int d\epsilon \int d\epsilon' \frac{f(\epsilon, T) - f(\epsilon', T)}{\epsilon - \epsilon'} \int_{BZ} d\vec{k} A_B(\epsilon, \vec{k}) A_B(\epsilon', \vec{k} + \vec{q}). \quad (2)$$

In equation (2), the k-space integral is extended to the first Brillouin Zone, $f(\epsilon, T)$ is the Fermi–Dirac distribution function and $A_B(\epsilon, \vec{k})$ is the Bloch spectral function (BSF). We recall here that the locus of the maxima of the BSF defines the band structure and, at the Fermi energy, $\epsilon = \epsilon_F$, the FS [16, 17]. The energy integrals in (2) can be transformed into a Matsubara energies sum and taking the low temperature limit picks up the Fermi energy contribution, i.e.

$$\chi(\vec{q}, T = 0) \sim \int_{BZ} d\vec{k} A_B(\epsilon_F, \vec{k}) A_B(\epsilon_F, \vec{k} + \vec{q}). \quad (3)$$

In equation (3) the FS nesting mechanism is shown: it is easy to realize that the self-convolution $\chi(\vec{q})$ takes large values (i) whenever the wavevector \vec{q} connects two points belonging to flat extended portions of the FS. However, the susceptibility can take large values also if (ii) \vec{q} connects small k-space regions, where the density of states is very high (Van Hove singularities) [4]. Equation (3) constitutes a prediction basis for the disorder–order transition as it allows us to envisage, from the electronic structure, the alloy ordering tendencies. The key quantity for our concerns is the wavevector at which the concentration waves susceptibility takes its maximum value, in the foregoing discussion it shall be simply referred to as \vec{q} . The theory predicts that if $\vec{q} \neq 0$ the alloy should order on decreasing T, if $\vec{q} = 0$ then its constituents should segregate. Although the CPA is unable to give correct charge transfers [18–22], the

nesting mechanism (i) is nevertheless able to explain the $L1_2$ phase in the CuPd system [10]. Also the CuPt $L1_1$ phase has been explained in terms of the FS, this time using the slightly different mechanism (ii) [4]: in this case the relevant Van Hove singularities are the closure of a hole pocket at X and the opening of a neck at L . All the above, of course, applies in the hypothesis that on lowering T no other competing effect would occur. We remark that predictions based on (3) can be reliable only when \vec{q} is close to a lattice commensurate value, otherwise one should take into account also the extra energy needed for the large strains required by the ordering transition.

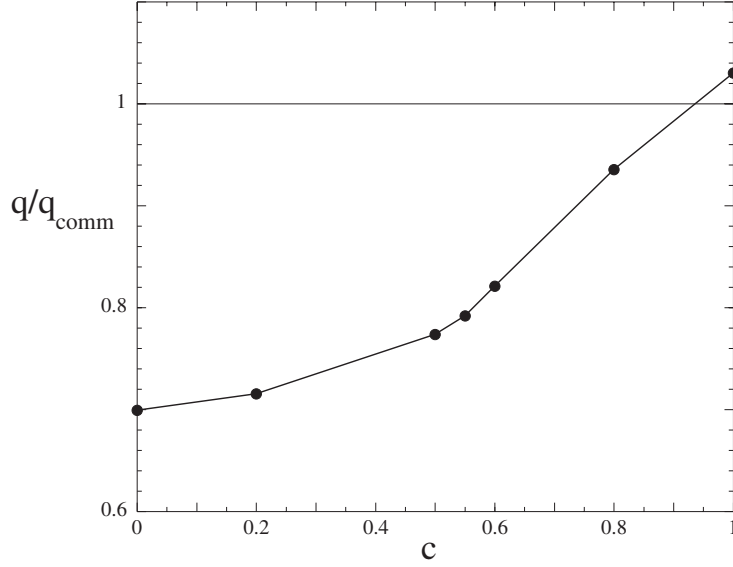


Figure 1. The nesting vector, q along the $[1, 1, 0]$ direction against the Cu concentration in the fcc $\text{Cu}_c\text{Pd}_{1-c}$ random alloy.

In this letter we analyse the FSs of the CuPd alloy system. Details of our method for alloy FS calculation can be found in [17]. We have employed effective Kohn–Sham alloy potentials determined within the local density approximation of the density functional theory using the Korringa–Kohn–Rostoker multiple scattering theory in conjunction with the CPA, an account of our method can be found in [23]. Since the direction $[1, 1, 0]$, or ΓK , is expected to induce the $[0, 0, 1]$ ordering in fcc CuPd solid solutions [7, 10], we have studied the FS nesting vector along ΓK as a function of the concentration and plotted the results in figure 1. The horizontal line represents the commensurate value, $\vec{q}_{comm} = (2\pi/a)[\frac{1}{2}, \frac{1}{2}, 0] \equiv (2\pi/a)[0, 0, \frac{1}{2}]$, where the last equality follows subtracting off a reciprocal lattice vector. This value is required to obtain a superlattice along the $[0, 0, 1]$ direction, with the same geometrical fcc lattice. This, for $c = 0.50$, corresponds to the $L1_0$ structure with $c/a = 1$, or the $L1_2$ structure if the concentration is 0.75 or 0.25. As one can see, the nesting vector is commensurate only at $c \simeq 0.90$. This is consistent with the experimental phase diagram [2], which, for the $L1_2$ phase, reports the *overstoichiometric* value $c_{MAX} \simeq 0.85$; while, at the stoichiometric concentration, the α'' structure is found. The last is a LPS, i.e. a $L1_2$ based lattice where the sequence of A and AB planes is superimposed by antiphase domains with a much larger periodicity. The last could arise from the beating of the nearly-two-layer periodicity required by the nesting vector and the two-layer periodicity typical of the $L1_2$ phase. In the region around $c = 0.25$ no $L1_2$ phase is observed and we relate this fact to the large incommensurability of the nesting vector.

All the above results can be interpreted as a confirmation of our working hypothesis that the predictivity of equation (3) is enhanced by the commensurability of the nesting vector.

The most intriguing region of the alloy phase diagram, however, is that around $c = 0.50$, where the B2 phase is observed whilst the relevant nesting vector is largely incommensurate. The bainitic transition from the fcc solid solution to the B2 phase cannot be explained simply in terms of the concentration waves picture. In [5] we proposed a non-perturbative attack to the study of the interplay between concentration fluctuations and lattice deformations and pointed out the preeminent role played here by charge transfers. Very briefly, since the concentration waves picture is satisfactory in the Cu-rich region [9, 10] and the ordering at the equiatomic concentration still occurs along the $[0, 0, 1]$ direction, one can imagine that the lattice strain is related *both* to the concentration fluctuations and the charge transfers. In fact, if the ordering occurs by alternating A^- and B^+ planes, an electrostatic attraction could shrink the lattice along the same direction, increasing the chance of having a Bain transition [5] from a fcc to a bcc geometrical lattice.

At this stage we need to go back to equation (3). The FS nesting can enhance the susceptibility of concentration fluctuations as well as fluctuations of other physical quantities, this is the reason why we have omitted the proportionality factor in (3), which, actually, depends on *which* physical quantity. If we wish to study charge or magnetization waves the appropriate factors can be obtained from the Friedel [24] or the Ruderman–Kittel–Kasuya–Yosida [25] theories respectively, but, again, the relevant wavevectors would be given by equation (3). This means that where *concentration waves* are expected, one has to expect *charge waves* too. In other words, when the chemical ordering increases, also the charge transfers grow, *due to the same Fermi liquid mechanism* and new phases can stabilize because of the gain in the electrostatic energy, although other repulsions (namely due to the band energy) should be taken into account. Since the charge transfers are expected to grow with the number of unlike neighbours [19–21, 26, such an effect must be greater *at* $c = 0.50$. Thus, because of the chemical and charge orderings, an electrostatic attraction arises between Cu^- and Pd^+ planes, providing the work necessary to a lattice shrink along $[0, 0, 1]$ ¹. In [5] we studied the total energy and the charge transfer against the c/a ratio for this alloy in the ordered, partially ordered (long range) and disordered phases at constant volume. For the random alloys we found two local minima, corresponding to fcc and bcc, separated by a relatively high energy barrier; for partially ordered alloys the barrier was greatly reduced and, eventually, for the ordered alloys the fcc minimum disappeared. These trends are clearly related to the increase of the charge transfer with chemical ordering.

What remains to be understood is why the maximum transition temperature occurs at the overstoichiometric concentration $c_{MAX} = 0.60$ and not at the equiatomic concentration as the charge transfer mechanism would suggest. In a recent paper, Donato *et al* [27] published an embedded atom Monte Carlo calculation for CuPd. They found c_{MAX} to occur at the stoichiometric concentration and their calculated coexistence line is symmetric around $c = 0.50$. As their calculation correctly accounts for entropic effects, we argue that the observed *asymmetry* of the coexistence curve must have an electronic origin. Furthermore, since the charge transfer is maximum *at* $c = 0.5$, the explanation must be envisaged in some mechanism *in competition* with the electrostatics.

To make further progress, we calculated the FSs for body centred tetragonal (bct) random alloys on varying the c/a ratio at constant unit cell volume. The directions $[1, 1, 0]$ of the fcc lattice correspond, in the new lattices, to the non-equivalent $[1, 0, 0]$ and $[1, 1, 2]$ directions.

¹ It is worth noting that, opposite to what is usually found in electronegativity tables, in CuPd alloys electrons transfer from Pd to Cu according to our results, other theoretical calculations [18, 22] and the Auger core shift measurements of [26].

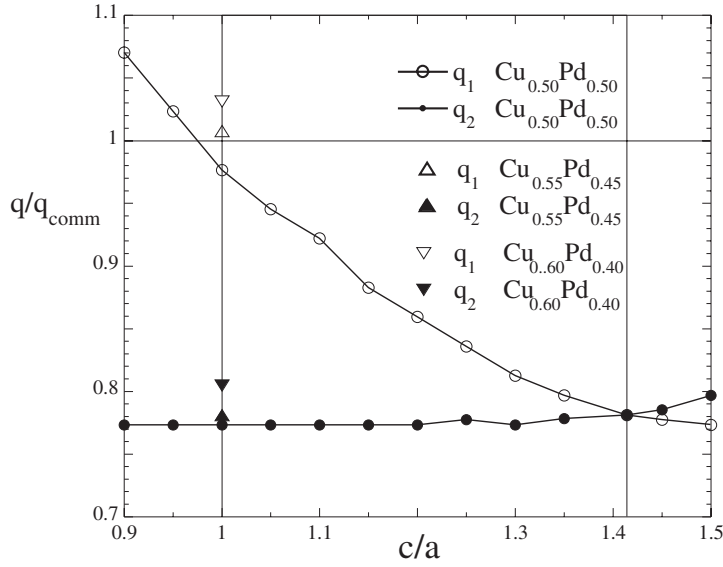


Figure 2. The nesting vectors q_1 and q_2 , along the $[1, 0, 0]$ and $[1, 1, 2]$ directions respectively, in units of the corresponding commensurate values (see the text) against the tetragonal strain, c/a , along the Bain path at constant volume, $V_c = 185.07 \text{ au}^3$ (where au denotes atomic units), for CuPd alloys. The vertical lines correspond to the bcc ($c/a = 1$) and to the fcc ($c/a = \sqrt{2}$) lattices.

Thus, corresponding to the fcc \vec{q}_{comm} , now we have *two* vectors: $\vec{q}_{comm,1} = 2\pi[\frac{1}{2a}, 0, 0]$ and $\vec{q}_{comm,2} = 2\pi[\frac{1}{4a}, \frac{1}{4a}, \frac{1}{2c}] \equiv 2\pi[\frac{1}{4a}, \frac{1}{4a}, 0]$. The nesting vectors, along the above directions, \vec{q}_1 and \vec{q}_2 , are displayed in figure 2. Interestingly, but not surprisingly on the basis of our working hypothesis, we see that, close to the bcc lattice, \vec{q}_1 approaches the commensurate value. This, indeed, supports the idea that $[1, 0, 0]$ ordering in the CuPd equiatomic alloy can be favoured by FS nesting only if one has, at the same time, a substantial lattice deformation. Of course, the conclusion that the B2 phase is the equilibrium one at $c = 0.5$ cannot be drawn within the concentration functional theory framework, not even if the elastic energy is included in the functional, since the actual deformation is by far too large to be treated perturbatively and full total energy calculations are required [5]. On the other hand, the small residual differences between the calculated \vec{q} and the ideal commensurate values must not be forgotten. These mismatches are an example of what we like to call a FS *frustration* effect. Nature has envisaged various ways to reduce this kind of frustration: as we have already seen a similar situation leads to LPSs in the Cu-rich part of the phase diagram, under other circumstances it could lead to tetragonalization. In the present case, the energetic cost that has to be paid in creating antiphase domains would be too large, just because of the large charge transfer. On the other hand, our figure 2 suggests the possibility of tetragonalization, namely with $c/a \simeq 0.97$. This, however, would increase the electrostatic energy by increasing the first (unlike) neighbours distance and reducing that of the second (like) neighbours. Our total energy calculations show that tetragonalization does not occur (see figure 1(a) in [5]), evidently, in this case, the electrostatic gain overcomes the FS frustration. On the basis of the above arguments, we may ask whether a modification of the concentration could reduce the FS frustration. The question is answered in figure 2, where we have also plotted the nesting vectors for the bcc $\text{Cu}_{0.55}\text{Pd}_{0.45}$ and $\text{Cu}_{0.60}\text{Pd}_{0.40}$ alloys. For $\text{Cu}_{0.55}\text{Pd}_{0.45}$ \vec{q}_1 falls just on top of the commensurate value. This proves that an increase of c over the stoichiometric value 0.5 improves the stability of the low-temperature phase and is consistent with the experimental

phase diagram that gives $c_{MAX} = 0.60$. We think that this is neat evidence that the extremal vectors of the FS, or, better, the competition between FS frustration and charge transfer, explain the asymmetry of the fcc-B2 coexistence line in the CuPd phase diagram.

In conclusion our results provide evidence that the electronic structure of a random alloy contains the seeds of the low-temperature ordering phenomena that occur in CuPd, including the peculiar fcc-B2 transition. In all the transitions the FS plays a fundamental role, providing the driving forces for charge and chemical orderings, through the nesting mechanism. Finally, the FS frustration that arises from the incommensurability with the lattice of the nesting vector \vec{q} is responsible for the observed asymmetry of the B2 and $L1_2$ phases and explain the fact that the corresponding coexistence curves have *non-stoichiometric* critical concentrations. The inclusion of the last mechanism turns out to be crucial for the accurate theoretical determination of the alloy phase diagram.

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