THE STABILITY OF LONG PERIOD SUPERSTRUCTURES
WITHIN THE ISING MODEL FRAMEWORK

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Abstract

Long Period Superstructures owe their stability to the interaction between the Fermi surface and the Brillouin zone boundaries. This is reflected in the fairly long range interactions that are needed to compute the free energy of these phases with lattice models. We present the results of a mean field computation for the Cu-Pd system and will indicate how the more accurate Cluster Variation Method could be used for these structures with large unit cells.
Introduction

A one-dimensional long period superstructure (LPS) can be thought of as a simple ordered superstructure that is anti-phased along one direction in a periodic and regular [1] fashion. The sequence of antiphase boundaries is regular and well-determined. The presence of these long period superstructure as equilibrium phases in many binary alloys has become well-documented. Using x-ray diffraction and electron microscopy, modulated superstructures have been detected in noble metal alloys as well as in transition metal systems. Table 1 gives an (undoubtedly not complete) overview of the binary alloys in which long period superstructures of A_3B type have been observed.

Figure 1 illustrates how a one-dimensional LPS of A_3B composition can be constructed graphically by modulating an L1_2 superstructure with a planar square modulation wave [1,13]. Whenever the modulation function changes sign, an anti-phase boundary is introduced by translating one part of the crystal with respect to the other by the vector (0,1/2,1/2) (if x is the modulation direction). The structures are labeled by their Fisher and Selke notation which specifies, between angular brackets, the sequence of domain lengths between anti-phase boundaries. In this notation L1_2 (the unmodulated structure) becomes <∞>, DO_{22} is written as <1> and DO_{23} as <2>.

The occurrence of LPS in alloys seems to be more the rule than the exception, and it is likely that many alloy systems could be added to the list in Table 1 if they were subjected to the careful experimenting that is required to find these superstructures. In this paper we will discuss the origin of stability of long period superstructure phases, both from an electronic point of view and within the context of a lattice model that can be used to perform thermodynamic calculations.

Stability of LPS

The original explanation for the occurrence of these large unit cell structures is due to Sato and Toth and relies on the assumption that the net electron energy is lowered when the Fermi surface touches the Brillouin Zone boundary. When this is not possible in the simple ordered alloy, LPS form, thereby creating new Brillouin zone boundaries that make contact with the Fermi surface.

The Sato and Toth theory correctly associates the stability of the LPS with the energy of the valence electrons, and despite its apparent simplicity, it has had a remarkable amount of success in explaining observations in alloys that exhibit long period superstructures [14]. However, the theory has also received strong criticism, especially from bandstructure theorists claiming that, in three dimensions, stabilization of the Fermi surface at a Brillouin zone boundary is only appreciable for Fermi surfaces that are strongly
Table 1: Some of the binary systems in which long period superstructures have been discovered.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>COMPOSITION</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Au</td>
<td>30-38% Au</td>
<td>(2)</td>
</tr>
<tr>
<td>Cu-Pd</td>
<td>18-30% Pd</td>
<td>(3,4)</td>
</tr>
<tr>
<td>Cu-Al</td>
<td>22-24% Al</td>
<td>(5)</td>
</tr>
<tr>
<td>Cu-Pt</td>
<td>24-26% Pt</td>
<td>(6)</td>
</tr>
<tr>
<td>Au-Zn</td>
<td>19-26% Zn</td>
<td>(7)</td>
</tr>
<tr>
<td>Ag-Mg</td>
<td>21-28.5% Mg</td>
<td>(8)</td>
</tr>
<tr>
<td>Pt-V</td>
<td>23-25% V</td>
<td>(9)</td>
</tr>
<tr>
<td>Pd-Mn</td>
<td>25% Mn</td>
<td>(10)</td>
</tr>
<tr>
<td>Au-Cd</td>
<td>24.5-25.5% Cd</td>
<td>(6,11)</td>
</tr>
<tr>
<td>Al-Ti</td>
<td>27.5-28.5% Ti</td>
<td>(12)</td>
</tr>
</tbody>
</table>

Fig. 1: A long period superstructure can be constructed from an L12 by modulating it with a square wave. The structure is denoted by specifying the length of non anti-phased domains in the unit cell. In this example the modulation function has wavelength $M=5/3$ (in units of the FCC lattice parameter) and the structure is $<221>$. 
deformed from the spherical shape [15]. Moreover, in the Sato and Toth theory, the modulation period \( M \) is only determined by the position of the Fermi surface; and the model cannot explain the observed change of period with temperature, nor the difference between systems with diffuse or well-defined anti-phase boundaries.

**The Ising-Alloy Model**

Due to the relative success of lattice models in reproducing coherent alloy phase diagrams, it seemed logical to apply them to the study of the long period superstructure phenomenon. The ANNNI (Axial Next Nearest Neighbor Interaction) model [16], originally devised to study the modulations of ferromagnetic order in magnetic materials like CeSb, showed that the origin of the long periods lay in the competitiveness of the spin interactions along one direction. Although this idea can be transferred to long period chemical order in alloys, the ANNNI model is not fully applicable to describe the thermodynamics of binary alloys as it considers ordering on a tetragonal lattice instead of the fcc lattice that is common to most alloys. In the next section we will briefly describe the general Ising Hamiltonian that is used in alloy theory and discuss the aspects that are relevant for the study of long period superstructures.

In the Ising model, the configuration of the alloy is described by a distribution of spins on a lattice. The spin variable at a site of the lattice \( \sigma_i \) is either +1 or -1 depending on whether that site is occupied by an A or B atom. Although the Ising model may seem like an over-simplified representation of the real alloy, it can actually be shown that, without any significant approximations, the total alloy-energy can be cast into an extended Ising Hamiltonian of the form [17]

\[
E = V_0 + \sum_{i} V_i \sigma_i + \sum_{i,j} J_{ij} \sigma_i \sigma_j + \sum_{i,j,k} \epsilon_{ijk} \sigma_i \sigma_j \sigma_k + \ldots
\]  

(1)

The \( V \)'s are effective cluster interactions (ECI) and can be obtained from total energy computations at zero \( K \). Note that in addition to the common ‘pair interaction term’ the energy expression (1) also contains constant and linear terms as well as multiplet interactions. Eq. (1) only becomes practical when it is truncated. The distance at which the interaction can be set to zero depends on the system under study. Some insight in the minimal interaction set to describe systems with LPS phases can be gained from characterizing the stable structures at zero \( K \) (ground states). When the expansion for the energy (Eq. 1) is truncated, the ground states can be found exactly as a function of the effective cluster interactions [17]: In most ab initio computations for binary alloys only interactions up to the second nearest neighbor distance in fcc are used. Occasionally ECI up to fourth nearest neighbor distances have been retained [18] to ensure proper convergence of Eq. (1). Fifteen possible ground state structures [19, 20] can be obtained when pair and multiplet interactions spanning the first and second nn distance in fcc are used in the energy expansion. Only the two simplest LPS, Li2 and DO22, are in this set of 15. The number of possible ground states increases drastically when the interaction range
is extended to fourth nearest neighbors. However, no new Long Period Superstructures are obtained. The first interaction to stabilize additional LPS as ground states is the eight nearest neighbor.

Computing the free energy of an Ising model with such long range interactions is a formidable challenge, except in the Bragg Williams theory, the simplest of statistical approximations. In the next section we will present the results of such a Bragg Williams model applied to the Cu-Pd phase diagrams.

The Cu-Pd One-Dimensional Long Period Superstructure Phase Diagram

When only effective pair interactions are retained in equation (1), the formula for the energy can be Fourier transformed to $k$-space:

$$ E = \sum_k \mathbf{V}(\mathbf{k}) \left| \Gamma_k \right|^2 $$

(2)

where $\Gamma_k$ and $\mathbf{V}(\mathbf{k})$ are respectively, the Fourier transform of the site occupation variables, and the Fourier transform of the effective pair interactions. Taking the mean field average of Eq. (2) and combining it with an ideal solution entropy on the different sublattices of the ordered structure results in a Bragg Williams model for the free energy.

When only one dominant $\mathbf{k}$ vector is chosen, this hybrid mean field theory is equivalent to the concentration wave technique [24]. Using this hybrid mean field theory, the appearance and stability of LPS can be explained in terms of the shape of the effective interaction $\mathbf{V}(\mathbf{k})$ [25,26]: At low temperature, the stable structure will have most of its ordering intensity ($\Gamma_k^2$) located near the minimum in $\mathbf{V}(\mathbf{k})$, although usually not in the minimum. As the temperature increases, phase transitions to other structures with more ordering intensity closer to the $\mathbf{V}(\mathbf{k})$ minimum take place.

Stocks, Gyorffy and Nicholson [27] have computed $\mathbf{V}(\mathbf{k})$ for Cu-Pd by means of the KKR-CPA-$\mathbf{S}_2\mathbf{k}$ method. Fig. 2 shows the part of $\mathbf{V}(\mathbf{k})$ between (010) and (1/2 1 0) for three alloy compositions. With this effective interaction as input to the Bragg Williams model we computed the long period superstructure phase diagram for Cu-Pd. The result is shown in figures 3a and 3b.
Most of the quantitative features of the phase diagram are in good agreement with experiments: The Li$_2$ structure is stable at low Pd concentrations. In alloys with higher Pd content one-dimensional LPS are stable. The modulation wavelength $\lambda$ decreases with increasing Pd concentration, in agreement with experimental observations [3,4]. In the range 0.24 < $c_{\text{Pd}}$ < 0.34 the wide $\text{k}$-$\text{l}$ LPS phase fields that are computed are exactly the ones that are observed: The $<3>$ phase around $c_{\text{Pd}}$=0.3 and the $<4>$ phase at $c_{\text{Pd}}$ =0.25. For $c_{\text{Pd}}$ < 0.24 we obtain structures with higher modulation periods ($M$=5, 5.5, 6). The phase fields of these structures is very narrow and does not reach zero $K$. We were not able to obtain the structures with very large modulation wavelengths ($M$>10) that are observed in [3] in the range $c_{\text{Pd}}$ < 0.2. This is likely due to the very approximate nature of the Bragg Williams entropy.

The qualitative agreement between the computed sequence of LPS and the experimentally observed one is probably the best that one can expect from a mean field theory. The maximum in the order-disorder transition temperature at 20% Pd in fig. 3 is the result of the strong concentration dependency of $\text{V}(\text{k})$ and masks one of the problems that is usually associated with a Bragg Williams computation on the fcc lattice: With composition independent interactions the transition temperature for all ordered phases is maximal at AB stoichiometry [22], in qualitative disagreement with the more accurate Cluster Variation Method result [23].
Fig. 3: a) phase diagram as calculated within the Bragg Williams approximation. Phases with modulation period larger than 4 are not labeled because their phase region is very small, but they can be identified on the enlargement in Fig 3b. The dashed line represents the ordering spinodals.
b) enlargement of the low Pd region: The three phase equilibrium $L1_2 - \alpha' - \langle 6 \rangle$ is approximately at the maximum of the order disorder transition so that the two phase regions between the disordered and ordered phases are very small.

The Cluster Variation Method and Long Period Superstructure

A better computation of the free energy of LPS phases could be provided by the Cluster Variation Method (CVM). In the CVM all correlations within some maximal cluster(s) are treated correctly. The CVM free energy function is minimized with respect to all these correlation functions. Correlations that extend outside the maximal cluster are neglected. It has been common practice to include in the expansion for the internal energy (eqn.1) only interactions that are inside that maximal cluster. For nearest neighbor interactions on the fcc lattice, the smallest maximal cluster that gives a good CVM free energy is the tetrahedron. For interactions up to second nearest neighbor the maximal clusters are the tetrahedron and octahedron. The required clusters grow rapidly as the interaction distance is extended, as do the number of variational parameters in the CVM free
energy. Two sets of maximal clusters can be used to incorporate fourth nearest neighbor interaction. The $13+14$ point cluster approximation (fig 4a) leads to a CVM with 742 correlation functions. Alternatively one can use the $13+10+10$ point clusters (Fig. 4b) with 'only' 371 correlation functions but a more complicated entropy expression. In any case, extending the CVM in this way to incorporate eight nearest neighbor interactions (as required to stabilize the $<3>$ phase as a ground state in Cu-Pd), would lead to an excessive number of correlation functions. Even if such a CVM free energy could be constructed, minimizing it would be virtually impossible.

![Fig. 4a: 14 + 13 point CVM approximation on the FCC lattice](image)

![Fig. 4b: 13 + 10 + 10 point approximation on the FCC lattice](image)

The solution might be in decoupling the energy and entropy expansion in the CVM free energy. A relatively 'small' cluster like the tetrahedron-octahedron can be used for the entropy. The correlations that extend outside this clusters and that are needed for the evaluation of the internal energy could be obtained by superposition from the correlation functions inside the maximal cluster. Pair correlations outside the maximal cluster would for example, be approximated by the product of the corresponding point correlation functions. Although this approach has been occasionally used [28] it has never been tested
carefully. It will probably yield acceptable results whenever the interaction for which this
superposition is applied, is unfrustrated. When the ground states of the system are
degenerate without the additional interaction, however, erroneous mean field features might
be present in the phase diagram. Research is currently underway to identify the conditions
under which the entropy expression can be truncated before the energy expansion.

Conclusion

Long period superstructures are stabilized by the interaction between the Fermi
surface and the Brillouin zone boundaries. This effect is responsible for the fairly long
range effective interactions in the Ising model. To stabilize long period superstructures as
ground states (apart from L12 and DO22) interactions over at least the 8th nearest neighbor
distance need to be incorporated, which makes the statistical thermodynamics models that
are used to compute the phase boundaries much more complex. Computations have only
been performed with mean field theory where long range interactions are effectively
mapped back into the unit cell. Although the sequence of long period superstructures in the
computed Cu-Pd phase diagram is generally in agreement with experiments, we expect that
better statistical mechanical models, like the CVM or Monte Carlo, could give a more
correct phase diagram topology, especially for the structures with high modulation
wavelength where the Bragg Williams theory seems to fail.

Acknowledgements

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