<100>* ORDERING WAVE AMPLITUDE COUPLING IN THE A1→L1$_2$ REACTION

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ABSTRACT

Recently, it has been suggested that relatively long-lived ordered states can develop in reactions involving two or more order parameters. These states are termed pseudostable states and correspond to saddle points in the free energy surface. The A1 (FCC) → L1$_2$ reaction involves the independent growth of three concentration wave amplitudes, corresponding to each of the <100>* k-space points. It is suggested that L1$_0$ pseudostable states could form during this reaction, under suitable thermodynamic and kinetic conditions. The range of structures possible by varying the <100>* amplitudes are given. A discussion of the microstructures that are likely to be observed if such a state were to be encountered is given. A fourth-order Landau expansion is developed, using these amplitudes as variables. The stabilities of all L1$_0$ states within this model are derived and tabulated. Under the right conditions, this expansion gives saddle points corresponding to L1$_0$ states.
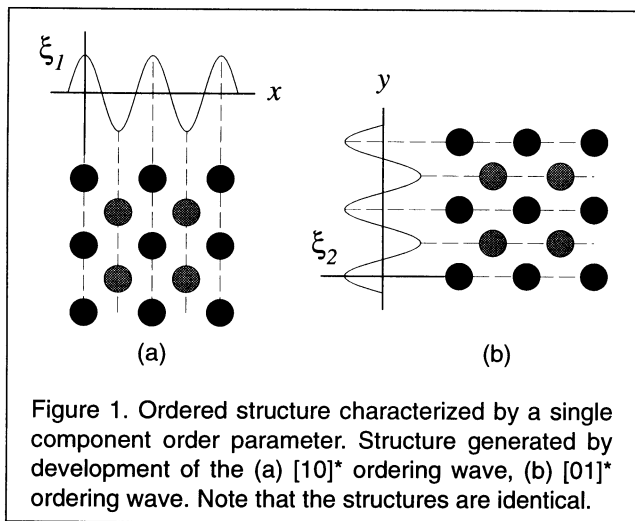
1. INTRODUCTION

Alloy properties are generally altered indirectly by changes in their microstructures, which in turn are altered by changes in their processing conditions. The relationships between processing and microstructures then comprises fully half of the alloy development problem. With the advent of the high speed computers, it has become possible to develop workable models of microstructural evolution that allow predictions to be made, à priori, as to the effects of variations of alloy and processing variables. Microstructural evolution studies can, for the first time, be studied in a systematic way by (1) identifying the regimes of alloy behavior in terms of these variables and (2) performing simulations of microstructural evolution in each of these regimes in order to determine the effects of each variable. This work attempts to advance the science by identifying a particular set of regimes of microstructural evolution: those in which the atomic order parameter has several degrees of freedom so that several different structures may be produced during the evolution of long range order.
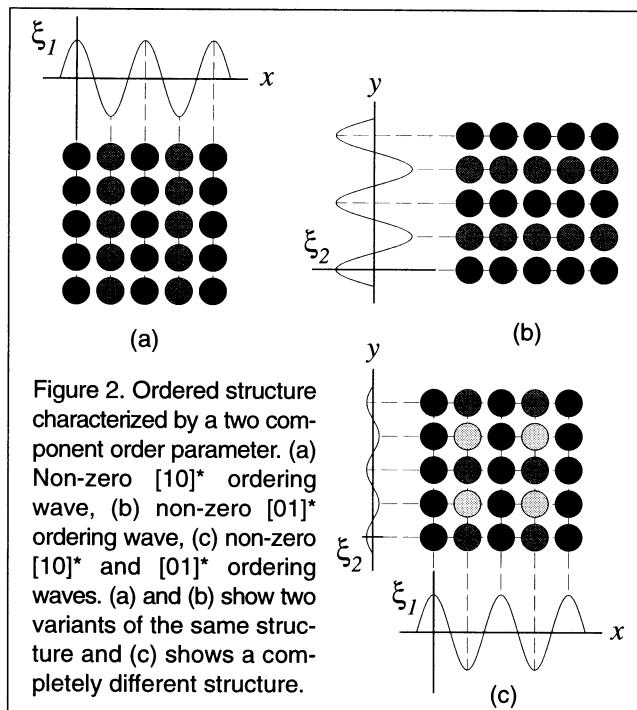
Thermodynamic analyses have been successfully used in the past to identify regimes of reaction behavior in systems that exhibit simultaneous ordering and phase separation.[Sof89; Kha88; All76; All82] These results can, and in some cases, have been used as a basis for microstructural evolution simulations.[Che91a; Che91b] The thermodynamic approach was initiated by Allen and Cahn,[All76; All75] to explore the existence of simultaneous ordering and phase separation in the Fe-Al system. The free energy of the solid solution was expanded into a Landau series[Lan80] in order parameter and predictions made as to the existence of atomic ordering followed by phase separation of the ordered product. Experimental studies have demonstrated that the predictions of Allen and Cahn were correct.[Sof81] Kubo and Wayman[Kub79] examined simultaneous ordering and phase separation in the second order BCC→B2 reaction, by using the static concentration wave (SCW) model.[deF71; Kha83] Khachaturyan, Lindsey, and Morris,[Kha88] applied the SCW model to the metastable first-order $\alpha \rightarrow \delta'$ (A1→L1$_2$) reaction that occurs in the Al-Li system[Mur88] and predicted a complex cascade of reactions that could occur because of the development of thermodynamic instabilities. L.Q. Chen, et al.,[Che91a; Che91b] performed microstructural evolution simulations in 2-d crystals with thermodynamic parameters chosen so as to reproduce the conditions necessary for coupled ordering and phase separation and observed many of the reaction features predicted by the thermodynamic analyses.

Thermodynamics as a method of predicting simultaneous ordering and phase separation reaction regimes was systematized by Soffa and Laughlin[Sof81; Lau88] by developing a heuristic approach by considering free energy curve geometries that were possible for each

Figure 1. Ordered structure characterized by a single component order parameter. Structure generated by development of the (a) [10]* ordering wave, (b) [01]* ordering wave. Note that the structures are identical.

system. These predictions were compared with model computations by Simmons and Laughlin[Sim92a] and by Simmons,[Sim92b] using the static concentration wave model. For a more complete review of simultaneous ordering and phase separation, the reader is referred to the work by Laughlin and Soffa.[Lau88]

The essential feature of coupled ordering and phase separation reactions is that one reaction (ordering) proceeds orders of magnitude faster than the other (phase separation). It is possible to use thermodynamics to make predictions of reaction regimes in which the reactions proceed at roughly the same pace, such as the

Figure 2. Ordered structure characterized by a two component order parameter. (a) Non-zero [10]* ordering wave, (b) non-zero [01]* ordering wave, (c) non-zero [10]* and [01]* ordering waves. (a) and (b) show two variants of the same structure and (c) shows a completely different structure.

evolution of two types of atomic ordering. but there will always be a degree of uncertainty, since it will not be possible to say whether a reaction sequence *will* occur, only that it can. Additional considerations of kinetics must be made in order to determine this. Nevertheless, the thermodynamic approach can be applied to identify the regimes of possible reactions, but whose plausibility can only be determined by kinetic considerations.

Predictions based on thermodynamics of ordering, where two competing ordering reactions occurred simultaneously were made by Fultz and coworkers[Ful93; Kik92; Ful92] In the evolution of order in Fe-Al alloys near the 25% Fe composition, both B2 order as well as DO_3 order compete.[All75] By varying the alloy composition and temperature, Fultz observed long-lived states of B2 order, where the equilibrium phase diagram indicates that the DO_3 Fe_3Al phase should be the equilibrium one.[Ful92] This long-lasting state was explained as being due to the existence of a saddle point in the free energy surface, where B2 and DO_3 order parameters are regarded as independent variables. This condition corresponds to a state of low thermodynamic driving force for order evolution and had been termed 'pseudostable states' by Fultz and coworkers.

In the example cited above, there are two degrees of freedom, corresponding to the order parameters of the B2 and DO_3 structures. At this point, we wish to point out the distinction between order parameters with only one component and those with order parameters containing several components. In the one component order parameter, only one ordering wave characterizes the type of order, the degree of order being determined by the amplitude of this ordering wave. An example of a one component order parameter structure is shown in Figure 1. The disordered state has 4-fold symmetry, implying the existence of an ordering wave oriented 90° away from the one shown. However, inspection of Figure 1 shows that the structure described by either ordering wave would be identical.

On the other hand, Figure 2 shows a structure where this is not the case. Although the parent structure has a 4-fold axis, the ordered structure formed by the ordering waves related to each other by a 90° rotation are distinct, being variants of each other. Further, the superposition of these two ordering waves produces a completely different structure than either of the two variants. Thus, if the order parameter has several components, the state of order of the alloy is described by several ordering wave amplitudes, each being relatable to each other by the symmetry of the parent structure, but that can vary independently of one another.

The $L1_2$ structure is characterized by three components: the amplitudes of ordering waves characterized by $\mathbf{k} = <100>*$, $<010>*$, and $<001>*$,[Kha73] where
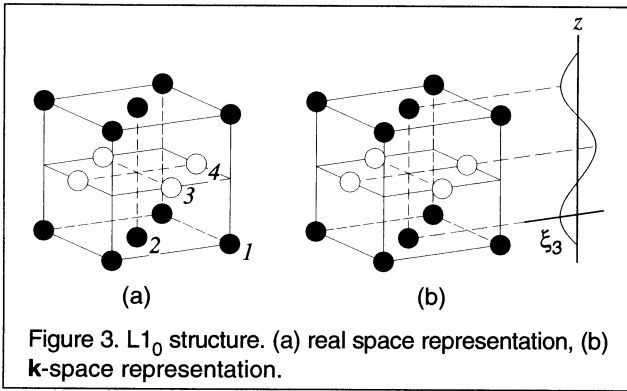
Figure 3. L1$_0$ structure. (a) real space representation, (b) k-space representation.

the asterisk is used to refer to the reciprocal lattice vectors describing the ordering wave vectors.

This work explores the possible existence of pseudostable states that could appear during the development of L1$_2$ order. In section 2, we will discuss the structures that can be formed by the independent variation of the three components of the <100>* order parameter. In section 3, we will discuss pseudostable states and the microstructures that would be expected to form as a result. Section 4, we will show that L1$_0$ pseudostable states are plausible in this system by developing a Landau expansion of the free energy that is consistent with the symmetry of the structures involved[Lan80; Izy90] and solving for the existence of stationary states. Section 5 will address some of the limitations of this treatment and section 6 will give a summary of the conclusions drawn from this work. We will limit our investigation to those cases where nucleation barriers are specifically neglected: only barrierless transitions will be considered. Our treatment will be a thermodynamic one which will, therefore, give necessary but not sufficient conditions for the appearance of pseudostable states. A kinetic model would be necessary in order to determine whether or not one would be encountered.

2. XI AND THE K-SPACE REPRESENTATION

In analyzing stability of ordered structures, there are commonly two representations employed of the structure. The most straightforward is the *real space* representation, in which the structure is divided into sublattices and the average compositions on each sublattice are the independent variables. This has the advantage of simplicity and clarity of expression. When analyzing stability of ordered structures, particularly against infinitesimal variations, the k-space representation is more frequently employed, since periodic structures will develop instabilities with respect to amplification of sinusoidal variations in composition, displacement,

or some other alloy parameter. The next section will discuss the k-space representation of the A1 → L1$_2$ reaction in more detail. The following section will discuss the various structures that can form as a result of the independent variation of the three components of the <100>* order parameter.
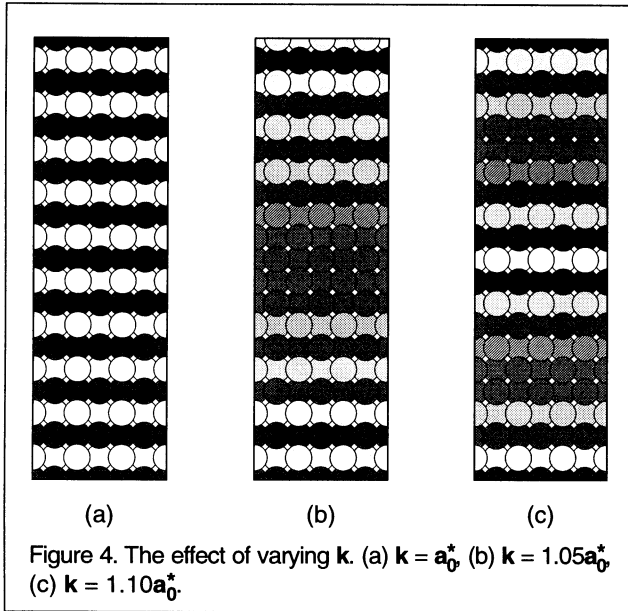
ξ-Space

Ordered structures may be described in terms of the site occupancies, for example, the L1$_0$ structure shown in Figure 3(a) may be described by specifying that $n_1 = n_2 = 1$ and $n_3 = n_4 = 0$, where the n_i's represent the occupation probabilities at site i. The crystal structure is then represented by specifying sites *1,2, 3*, and *4*, along with the values of site occupancy n_1, n_2, n_3, and n_4. This forms the basis of the real space representation, or the $C(\mathbf{r})$ representation. In the $C(\mathbf{r})$ representation, $\mathbf{r}$ is the independent variable, chosen to refer to a particular lattice site, and C is the dependent variable, reflecting the (already determined) average composition at that site.

The structure may be equivalently described in terms of the wavelengths and amplitudes of static concentration waves[Kha83] that would have to be superposed in order to give the same structure. In Figure 3 (b), the same structure is described by specifying that $\xi(000) = 0.5$, $\xi(001) = 0.5$, and $\xi(100) = \xi(010) = 0$, where $\xi(000)$ is the amplitude of the constant wave corresponding to $\mathbf{k} = [000]*$, and $\xi(100)$, $\xi(010)$, and $\xi(001)$ are, respectively, the amplitudes of the waves corresponding to $\mathbf{k} = [100]*$, $[010]*$, and $[001]*$. The crystal structure may then be described by specifying the values of $\mathbf{k}$: [000], [100]*, [010]*, and [001]*, along with their amplitudes $\xi(000)$, $\xi(100)$, $\xi(010)$, and $\xi(001)$. This is the k-space representation, which we may also refer to as the $\xi(\mathbf{k})$ representation. Here, the $\mathbf{k}$ vector is the independent variable, and the value of ξ is a function of that particular $\mathbf{k}$.

The k-space representation was originally proposed by Landau[Lan37] and subsequently developed by Khachaturyan,[Kha62] Cook and deFontaine[Coo69] and deFontaine.[deF79] It is more convenient when analyzing the stability of structures with respect to spinodal decomposition or ordering. Since it is our purpose to focus exclusively on barrierless mechanisms, we will use this representation. Many works have addressed themselves to the description of ordering reactions with the k-space representation,[Lan80; Kha83; Kha78] the majority of them have examined the roll of the k vector describing the structures formed. However, some additional works have addressed themselves to the roll of ξ.[Sim92b; Izy90; Guf73; Guf71; Kaj78]

Figures 4 and 5 show, respectively, the effects of variations in k and ξ on the structure for a single com-

Figure 4. The effect of varying $\mathbf{k}$. (a) $\mathbf{k} = \mathbf{a}_0^*$, (b) $\mathbf{k} = 1.05\mathbf{a}_0^*$, (c) $\mathbf{k} = 1.10\mathbf{a}_0^*$.

Figure 5. The effect of varying ξ. (a) $\xi_1 = 1.0c$, (b) $\xi_1 = 0.6c$, (c) $\xi_1 = 0.0$, (d) $\xi_1 = -0.5c$, (e) $\xi_1 = -1.0c$. c is the bulk compostion.

ponent order parameter. Variations in $\mathbf{k}$ change the periodicity which, in the case of Figure 4 is affected by the introduction of periodic antiphase boundaries. This affects the type of order, since the ordered structures are distinguishable from each other on the basis of the symmetry. Variations in ξ change only the degree of order. The distinction between ξ and $\mathbf{k}$ is similar to that between AM and FM radio signals, whereas with AM signals, the information is contained in the amplitude of the signal and with FM signals, the information is contained in the frequency. This may be an oversimplification, since with radio signals, it is the variation of amplitude and frequency that conveys the information, and in our case, it is the absolute magnitude of these that conveys the information. We address here the information contained in the amplitude of the concentration waves.*
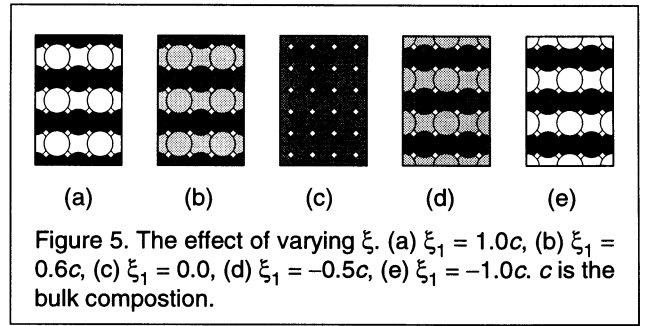
If attention is restricted to the <100>* ordering wave, the real space and $\mathbf{k}$-space descriptions can be related to each other by the following relations due to Khachaturyan:[Kha73]

$$n_1 = c + \xi_1 + \xi_2 + \xi_3 \tag{1a}$$

$$n_2 = c + \xi_1 - \xi_2 - \xi_3 \tag{1b}$$

$$n_3 = c - \xi_1 - \xi_2 + \xi_3 \tag{1c}$$

$$n_4 = c - \xi_1 + \xi_2 - \xi_3 \tag{1d}$$

where

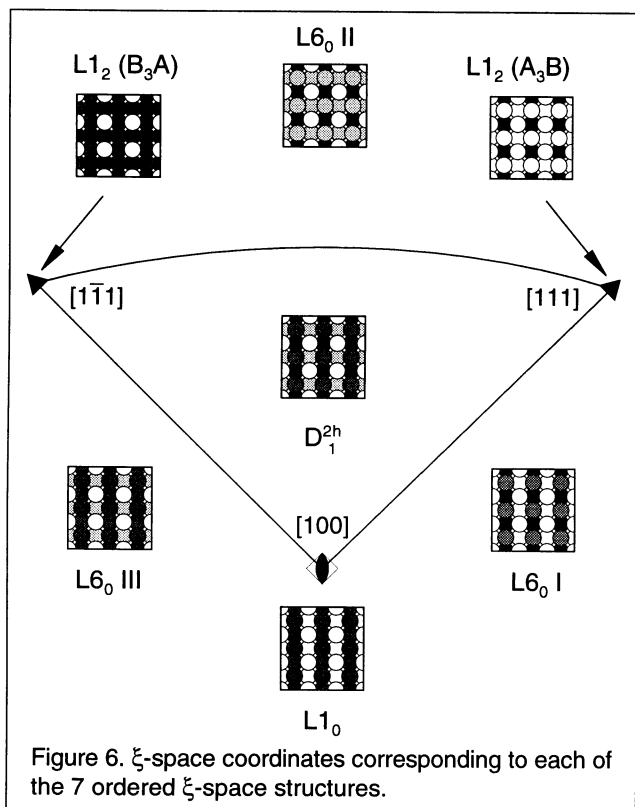 c is the bulk composition of the alloy.

As was eluded to in the introduction, many of the $\mathbf{k}$-space structures that have been studied so far are produced by a single concentration wave amplitude. From Equation (1), it is seen that there are in all three independent components of the order parameter for the <100>* ordering transition. Each of these amplitudes can vary independently of one another, allowing the appearance of a number of ordered structures, as illustrated in Figure 6. This independence also leads to a number of paths that may be taken during the ordering process. The following section discusses the range of structures that may be realized.

<100>* ξ-Space Structures

In all, there are eight structures that may be formed by differing values of ξ_i: A1 (FCC), two $L1_2$ structures, $L1_0$, three tetragonal $L6_0$ structures, and one orthorhombic structure. The A1 structure corresponds to the condition where all three amplitudes vanish. The $L1_2$ structure corresponds to the condition where all three amplitudes are non-zero, and equal. The $L1_0$ structure corresponds to the condition where only one amplitude is non-zero and the other two are zero. The $L6_0$ structure is obtained when one of the amplitudes is zero and the other two are non-zero and equal, and the orthorhombic structure corresponds to the condition that all three amplitudes are non-zero and unequal. All of these structures are shown in Figure 7 and are superposed on a ξ-space stereogram in Figure 6. In this figure, the relative values of ξ_1, ξ_2, and ξ_3 form the coordinate axes x, y, and z.

The difference in the two $L1_2$ structures is that one has a higher probability of atoms of type 'A' being found at the corners and those of type 'B' at the face center positions, while the other $L1_2$ structure has the opposite condition.

The $L6_0$ structure[Pea58] may be viewed as an ordering of the $L1_0$ structure, only with the two sites in
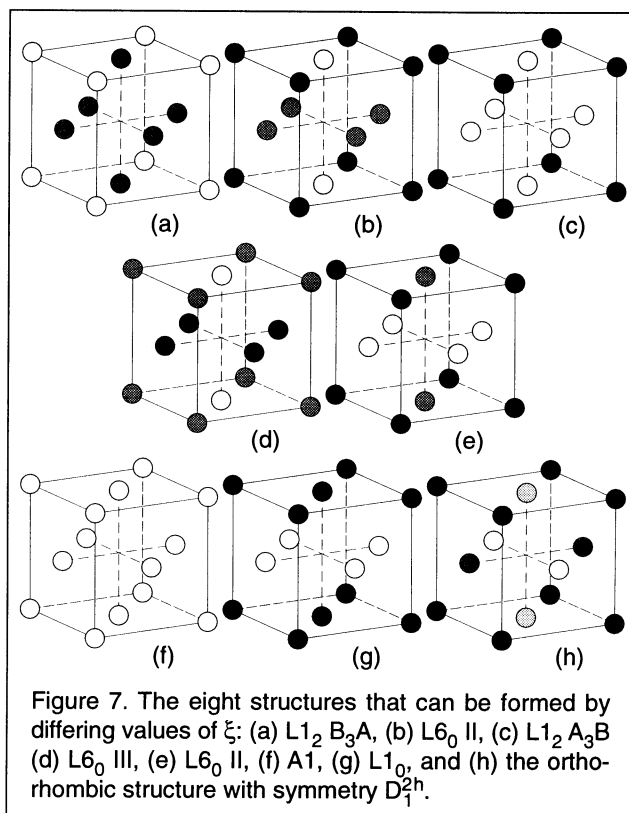
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* Our usage of ξ-space is similar to Gufan's usage of ε-space, except that we do not employ any normalization to the wave amplitudes.

Figure 6. ξ-space coordinates corresponding to each of the 7 ordered ξ-space structures.

Figure 7. The eight structures that can be formed by differing values of ξ: (a) $L1_2$ B_3A, (b) $L6_0$ II, (c) $L1_2$ A_3B (d) $L6_0$ III, (e) $L6_0$ II, (f) A1, (g) $L1_0$, and (h) the ortho-rhombic structure with symmetry D_1^{2h}.

the (001) plane of the conventional unit cell having a different occupation probability. Some evidence has been published that γ-TiAl may have this structure under certain conditions[Jac93] With the $L6_0$ structure, there are three different sublattice occupancies: two of the sublattices have the same occupancy. Depending upon whether these two have occupancy that is less than, intermediate, or greater than the occupancies of the other two, there are three distinguishable $L6_0$ structures.

The orthorhombic structure has all four sublattices differently occupied and represents the lowest symmetry structure realizable with <100>* ordering.

Of these, the A1, $L1_2$, and $L1_0$ structures have special symmetry in terms of ξ, so that the relative values of the ξ_i's are preserved when thermodynamic parameters such as pressure and temperature are varied.[Guf71] This can be seen from Figure 6, where the symmetries of these points in ξ-space are $\bar{4}3m$, $3mm$, and $2mm$, respectively. This symmetry is sufficient to guarantee that the angular coordinates in ξ-space are fixed. The other structures, the $L6_0$ and orthorhombic phase, do not have sufficient symmetry to fix their angular positions in ξ-space. The symmetries of these points are m and 1, respectively.

We would like to make one final note on the ξ-space structures. From Figure 6, we note that the *angular* coordinates in ξ-space determine the type of order, while the radial coordinate determines the degree of the ordering. In subsequent sections, we will change variables from (ξ_1, ξ_2, ξ_3) to a 'polar coordinate system,' (ξ_r, θ, ϕ), in which ξ_r represents the radial coordinate and θ and ϕ will have the usual meanings in polar coordinates.

3. TRANSFORMATION MICROSTRUCTURES

In what follows, we consider here a particular case of microstructural evolution that can occur, which is allowed by the multi-component order parameter. Specifically, we will investigate the possibility of forming a relatively long-lived non-equilibrium $L1_0$ state during the A1 $\rightarrow$ $L1_2$ reaction, before the final evolution to the $L1_2$ state.

Pseudostable States

The existence of pseudostable states was first proposed by Kikuchi, Mohri, and Fultz[Kik92] and later elaborated upon by Fultz in subsequent publications.[Ful93; Ful92] A pseudostable state corresponds to a point in a multi-dimensional order parameter space where the free energy surface develops a saddle point. This is used to explain the existence of long-lasting states that are neither stable nor metastable phases.

The argument is made as follows. To a first order approximation, the evolution of the order parameters follows the relation:[Ful93; Ful92]

$$\frac{d\eta_i}{dt} = \sum_j \gamma_{ij} \frac{\partial F}{\partial \eta_j} \qquad (2)$$

where

η_i is the i'th order parameter,

γ_{ij} are a set of kinetic coefficients and

t is time.

At any stationary point, where the gradient of the free energy vanishes, Equation (2) shows that there is no evolution of the order parameter. Using the usual assumptions of continuity, we can say that near a saddle point, there is very little evolution of the order parameter. It is not sufficient to have a saddle point in the free energy surface, however: the kinetics must favor the system evolving to that point in the first place. In other words, one mode of evolution must be faster than the others and this must lead to the pseudostable point. Once there, the system arrests for a time until sufficient evolution along one of the other modes is sufficient to provide enough driving force to cause the reaction to proceed more quickly.

The existence of pseudostable states is supported by both pair approximation cluster variation method computations as well as Monte Carlo simulations of the evolution of both short range and long range order during the development of B2 order.[Ful93] The pseudostable state concept was used as an explanation of observed transformation behavior in the Fe-Al and Fe-Co systems.[Ful92]

Microstructural Implications

In what follows, we will investigate the conditions for the appearance of saddle points in the free energy surface. The Landau expansion that we develop in the next section indicates the existence of a multitude of stationary points allowed by the symmetry of the <100>* ordering reaction. For reasons of clarity, we will only examine one of the simpler of the possibilities: that in which the A1 → L1$_2$ reaction proceeds via an L1$_0$ pseudostable state.

In this case, if there is sufficient strain energy due to the L1$_0$ transformation, we would expect a tweed structure, consisting of layers of twin related domains of L1$_0$, to be produced as a means of accommodating this strain energy.[Kha83] This would be characterized by {110} striations when imaged in TEM with **g** = <110>, along with <110>-oriented relrods. Higher resolution images, we would expect to show a mixture of twin related domains.

The tweed microstructure has been observed in sys-

tems exhibiting A1 → L1$_0$ reaction such as the CuAu[Aru67; Hir62; Yos72] and the CoPt systems[New51] and is characterized by <1$\bar{1}$0> relrods in the diffraction pattern that are normal to modulations parallel to {110} planes in the bright field image.[Tan66]

The reaction sequence that we then expect to see is (1) the disordered state, which is the quenched state, followed by (2) the development of a tweed contrast in TEM, followed by (3) development of the equilibrium L1$_2$ structure.

4. THERMODYNAMIC ANALYSIS

The suggestion was made in the last section that the A1 → L1$_2$ reaction could proceed via an intermediate state of L1$_0$ order, if the conditions were right. We will show in this section that this is reasonable, at least from consideration of the symmetries of the phases involved. We will perform a Landau expansion[Lan80] complete to fourth order. We will show that, for suitable choices of symmetry-allowed coefficients, saddle points do appear in the free energy surface corresponding to L1$_0$ states of order. The following section discusses the reasons for making the fourth-order expansion.

The Landau Exclusion Rules

It is well known that when a polynomial expansion of a large order is used to approximate a free energy surface there can be a number of 'instabilities' generated as a result of the changes in curvatures, just due to the power expansion. It is therefore desirable to limit the number of powers in the expansion as much as possible, in order to reduce this artifact.

According to Landau and Lifshitz,[Lan80] in order for a phase transition to be second order over a range of pressures and temperatures, the reaction must obey The 'Landau symmetry rules.' These rules are as follows:

1. The third-order invariant of the expansion must vanish identically,
2. the fourth-order invariant must be positive-definite, and
3. the ordered structure must correspond to a 'Lifshitz special point' in **k**-space.

According to Tolédano and Tolédano, no second order phase transition has ever been observed that violates the Landau symmetry rules,[Tol87] therefore, we expect that the first order nature of the A1 → L1$_2$ and A1 → L1$_0$ reactions would be a consequence of violations of these exclusion rules.

This is, in fact, the case. The first order nature of the A1 → L1$_2$ reaction is first order because of a non-zero third-order invariant and the A1 → L1$_0$ reaction is be-

cause of a negative value of the fourth-order invariant. We will discuss these two points briefly at the end of the following section. For now, we will simply say that, in order to account for the experimental observation that these two reactions are first order, the fourth order expansion is necessary and has the minimum necessary number of terms.

The Landau Expansion

Since the <100>* ordering reaction involves the independent growth or the ordering wave amplitudes, ξ_1, ξ_2, and ξ_3, the free energy is a function of these three variables. Fixing all other thermodynamic variables at a particular point and expanding the free energy in a Taylor's series about the disordered state gives:

$$f(\xi_1,\xi_2,\xi_3) = f_0 + \sum_i f_i\xi_i + \frac{1}{2!}\sum_{i,j} f_{i,j}\xi_i\xi_j +$$

$$\frac{1}{3!}\sum_{i,j,k} f_{i,j,k}\xi_i\xi_j\xi_k + \frac{1}{4!}\sum_{i,j,k,l} f_{i,j,k,l}\xi_i\xi_j\xi_k\xi_l + \dots \tag{3}$$

where

> f is the free energy of the homogeneous solution,
> f_0 is the free energy at the disordered state, and
> f_i is $\partial f/\partial \xi_i$, etc.

Equation (3) is general and describes the free energy of any three-component order parameter. We next simplify this relationship by (1) using the symmetry of ξ-space, (2) using the fact that the free energy function has exact differentials in ξ_i, and (3) retaining terms only up to fourth-order. The symmetry of ξ-space may be shown to be $\bar{4}3m$ from group theory[Tol81] or from a straightforward analysis of the types of structures that may be produced for each value of ξ_i.[Sim92b] For example, since the $\bar{4}3m$ point group has a 2-fold operator parallel to the ξ_3-axis, the structure represented by $\xi_1 > 0$, $\xi_2 = \xi_3 = 0$ is the same as that represented by $\xi_1 < 0$, $\xi_2 = \xi_3 = 0$, each being a distinct domain of L1$_0$. Thus $f(\xi_1, \xi_2, \xi_3) = f(-\xi_1, \xi_2, \xi_2)$ for all values of ξ_3, we can equate the expansion in terms of $+\xi_3$ to that in terms of $-\xi_3$ with the result that the coefficients of all terms that have odd powers of ξ_3 vanish identically. The application of all symmetry elements of the $\bar{4}3m$ point group reduces the number of independent constants in Equation (3) substantially. The fact that f has exact differentials implies that the order of differentiation is immaterial, which further reduces the number of constants.

Using these simplifications, we arrive the following expression:[Sim92b]

$$f = B\,\xi_r^2 + C\,\xi_r^3 + D\,\xi_r^4 + \dots \tag{4}$$

where

> $B = 1/2\,f_{11}$,
> $C = K_0 l_1 l_2 l_3$, K_0 being a constant and l_i being the i'th direction cosine[Nye57]
> $D = K_1 + K_2(l_1^4 + l_2^4 + l_3^4)$, K_1 and K_2 being constants, and
> $\xi_r = \sqrt{\xi_1^2 + \xi_2^2 + \xi_3^2}$

In order to analyze the stability, we make two further modifications. (1) We consider only temperatures at which an ordering instability occurs, so that the quadratic term in Equation (4) vanishes. And (2) in order that the order parameters remain bounded, the function must be positive for all sufficiently large values of order parameter. For this purpose, we add an isotropic sixth-order term to the expansion. This is for mathematical convenience and does not represent the totality of sixth-order terms that are allowed by symmetry, nor is it meant to imply that the fifth-order invariant vanishes identically. There are, in fact, a number of fifth-order terms allowed by symmetry.[Sim92b]

Making these approximations and substitutions gives the following simplified free energy relationship for a particular temperature and composition:[Sim92b]

$$f - f_0 \approx K_0\, l_1 l_2 l_3\, \xi_r^3 + K_1\, \xi_r^4$$

$$+ K_2\,(l_1^4 + l_2^4 + l_3^4)\,\xi_r^4 + \xi_r^6 \tag{5}$$

The first term on the right of Equation (5) gives the third-order invariant and the second and third terms give the fourth-order invariant. Referring to Equations (1) and Figure 7, we see that the L1$_2$ A$_3$B structure is represented by the [111], [$\bar{1}$11], [$1\bar{1}$1], and [$11\bar{1}$]-directions in ξ-space. This represents the extreme value in the third-order invariant: the L1$_2$ structure experiences the effect of the non-zero third-order invariant. We also make the observation this term is unimportant for the L1$_0$ structure, since two of the direction cosines will always be zero for any particular variant or domain. In this case, the first non-zero term is the fourth-order term. If this were positive, there would be no discontinuity in the equilibrium solution as the temperature is lowered to where B becomes negative[Ioo80] and the A1 → L1$_0$ reaction would be second order. Thus, we see that the L1$_2$ reaction is first order due to the violation of the Landau exclusion rule requiring that the third order invariant vanish and the L1$_0$ reaction is first order due to a violation of the exclusion rule requiring that the fourth order invariant be positive definite.

Stationary Solutions and Pseudostable States

Equation (5) has been solved analytically for equilibrium, as well as stability for both $L1_0$ and $L1_2$ phases,[Sim92b] by using the quadratic and cubic formulae. In all, there are 8 possibilities for the equilibrium solutions, in which specific combinations of roots are found. There are 4 possibilities for the stability, instability, or pseudostability of $L1_0$ solutions and 12 possibilities for the $L1_2$ solutions. We will not delve into the totality of solutions of Equation (5), but will concentrate on the stability solutions of the $L1_0$ structure in this section, since this is the possibility in which we are interested. In this section, we give a description of the steps taken in order to produce the solutions.

For a 1 component order parameter, the conditions for stable equilibrium are (1) $\partial f/\partial \xi = 0$ and (2) $\partial^2 f/\partial \xi^2 > 0$. For a three component order parameter, the analogous relationships are:

$$\frac{\partial f}{\partial \xi_1} = \frac{\partial f}{\partial \xi_2} = \frac{\partial f}{\partial \xi_3} = 0 \qquad (6)$$

and

$$\lambda_1 > 0, \ \lambda_2 > 0, \ \lambda_3 > 0 \qquad (7)$$

where

λ_1, λ_2, and λ_3 are second derivatives, $\partial^2 f/\partial \chi^2$, where χ represents a principal curvature direction.

Generally, the directions in which these second derivatives are taken will not be the ξ_i directions, but linear combinations of the ξ_i's. The solutions to Equation (6) that satisfy Equation (7) yield a 'phase diagram' in order parameter space. This has been calculated for ξ-spaces for many potentials by Gufan,[Guf71] including the $\bar{4}3m$ potential.

For pseudostable states, we must still satisfy Equation (6), but relax the condition that all three principal curvatures given by Equation (7) be positive. Since the product of the principal curvatures is the determinant of the *Hessian* matrix,[Str76] this determinant vanishes when one of the principal curvatures changes sign:

$$\begin{vmatrix} \dfrac{\partial^2 f}{\partial \xi_1^2} & \dfrac{\partial^2 f}{\partial \xi_1 \partial \xi_2} & \dfrac{\partial^2 f}{\partial \xi_1 \partial \xi_3} \\[2mm] \dfrac{\partial^2 f}{\partial \xi_1 \partial \xi_2} & \dfrac{\partial^2 f}{\partial \xi_2^2} & \dfrac{\partial^2 f}{\partial \xi_2 \partial \xi_3} \\[2mm] \dfrac{\partial^2 f}{\partial \xi_1 \partial \xi_3} & \dfrac{\partial^2 f}{\partial \xi_2 \partial \xi_3} & \dfrac{\partial^2 f}{\partial \xi_3^2} \end{vmatrix} = 0 \qquad (8)$$

Table 1. Stabilities of the $L1_0$ roots of the fourth order Landau expansion. The symbols under 'Stab' refer to the signs of the principal curvatures in the <100>-, <110>, and <$\bar{1}$10>- ξ-space directions, respectively.

Stab	Range of K-Values	
+++	$K_0 > 4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$	$K_0 > -4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$
++-	$K_0 < 4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$	$K_0 > -4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$
++-	$K_0 > 4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$	$K_0 < -4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$
+--	$K_0 < 4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$	$K_0 < -4/3 \ K_2\sqrt{-6 \ (K_1 + K_2)}$

The equilibrium solution to Equation (6) can be evaluated directly and yields:

$$\xi_1 = \pm\frac{1}{3}\sqrt{-6\left(K_1 + K_2\left(l_1^4 + l_2^4 + l_3^4\right)\right)} \qquad (9)$$

The stability of these solutions can be evaluated in the following manner. The individual terms of Equation (8) may be evaluated directly by differentiation. We then diagonalize the matrix, using the symmetry of the $\bar{4}3m$ point group. For the $L1_0$ structure, the state of order is represented by points along the <100>-directions in ξ-space. The symmetry of points along this direction is $2mm$,[Hah83] where the mirrors are parallel to {110} planes. Thus, we know that the principal directions in ξ-space for the $L1_0$ structure are along the <100>-, <110>-, and the <$\bar{1}$10>- ξ-space directions. We can immediately diagonalize Equation (8) by choosing these to be the new coordinate axes.

Substituting Equation (5) into Equation (8) and making these changes in coordinates, we obtain a 'diagonal' representation of the Hessian. From this, we obtain the values of the principal curvatures:

$$\lambda_1 = 30\xi_1^4 + 12\left(K_1 + K_2\right)\xi_1^2 \qquad (10a)$$

$$\lambda_2 = 6\xi_1^4 + 4K_1\xi_1^2 + K_0\xi_1 \qquad (10b)$$

and

$$\lambda_2 = 6\xi_1^4 + 4K_1\xi_1^2 - K_0\xi_1 \qquad (10c)$$

These represent the principal curvatures in the <100>-, <110>-, and <$\bar{1}$10>-directions, respectively. The surfaces at which each principal curvature given in Equations (10) vanishes may be found by substituting in the solutions of Equation (9) into Equations (10) and equating to zero. This yields the values given in Table 1.[Sim92b]

In Table 1, the stabilities of the equilibrium solutions of Equation (5) for the $L1_0$ structure. The symbols +++, ++-, etc. refer to the signs of the principal curvatures

in the <100>-, <110>-, and <$\bar{1}$10>-directions in ξ-space. The first row gives the relations between K_0, K_1, and K_2 produce an $L1_0$ structure that is stable against all variations. The second row gives these relations that produce a structure that is stable against variations in the <100>- and <$\bar{1}$10>-directions, but is unstable with respect to variations in the <110>-directions. An $L1_0$ state forming via this saddle point is expected to remain for a while, and then start to develop the A_3B type of $L1_2$ order. The same holds for the entry in the third row of this table, except that it would become unstable with respect to development of the B_3A type of order. The entry in the last row describes an $L1_0$ state that is unstable with respect to formation of any other ξ-space structure.

Thus, we see that alloys with the Landau coefficients described in rows 2 and 3 of Table 1 form $L1_0$ saddle points in ξ-space and that the assertions as to the formation of $L1_0$ as a pseudostable state are made more plausible. This does not constitute a guarantee, however. In the next section, we will discuss some of the limitations of our treatment.

5. LIMITATIONS

The conclusions made here, while quite general, are subject to some limitations, since we have made a number of approximations. We wish to list several of the more important limitations in this section.

First, the above analysis is a *thermodynamic* treatment. We cannot, by inspection, declare any of the steps of the reactions described herein as being faster or slower than any other. They will, no doubt, proceed at different rates, but a kinetic model would be necessary to make these predictions. The best that can be said of the above is that the existence of stationary points in the free energy surface is a *necessary*, but not sufficient condition for a pseudostable state. The additional necessary condition is that the kinetics favor the development of the transient ordered state corresponding to the pseudostable state.

Second, we have used a Landau expansion with a limited number of terms. On the one hand, this is good in that it does not produce artificial instabilities due to 'wiggles' in the power series. But on the other hand, it does not allow us to make quantitative comparisons of the degree of ordering predicted for any of the phases. We do believe that the qualitative features, such as the existence of pseudostable states are well within the level of approximations made.

We have also completely neglected the role of short range order as well as defects such as antiphase boundaries (APB's). It is known that the presence of APB's can affect transformations.[All76; Che91a]

Finally, we have employed a 'monochromatic approximation' in setting up the problem. That is to say, we have assumed that the growth rate of all concentration wave amplitudes except those corresponding exactly to the <100>* **k**-space points are zero. According to Lifshitz' analysis,[Lif41] the thermodynamic potential should be stationary, presumably a maximum, at these points. Our analysis applies in the situation where the growth rate is a maximum at the Lifshitz points and that peak broadening, due to growth of amplitudes whose **k**-values are close to, but not exactly equal to, the <100>* values. A more realistic approach would allow for this broadening, which we would expect to create a mixture of anti-phase domains of any particular structure formed, similar to that shown in Figure 4.

6. CONCLUSIONS

Reactions characterized by multi-component order parameters are qualitatively different from those characterized by single component order parameters. We have discussed these differences in terms of the possible structures that can be produced and one specific transformation scenario. We have developed a fourth order Landau expansion in order to show that this behavior is allowed by the symmetry of the structures involved. The following conclusions can be drawn:

1. The transformation behavior when the order parameter has multiple components is qualitatively different than when it has only a single component.
2. A multitude of structures are possible in the <100>* ordering reaction, each characterized by different relative values of the concentration wave amplitudes.
3. A possibility in which the $A1 \rightarrow L1_2$ transformation could proceed via an $L1_0$ pseudostable transition state was suggested and examined in more detail. The microstructural implications of such a reaction was discussed.
4. A thermodynamic analysis along the lines of that developed by Landau and Lifshitz[Lan80] was made and showed that such a transformation was allowed, when taking symmetry and thermodynamic constraints into consideration. These effects appear when a fourth order expansion in free energy was made, this being the minimum order required to account for the experimentally observed first-order nature of the $L1_2$ and $L1_0$ ordering reactions.
5. The values of the coefficients of the Landau expansion producing each possible stable, pseudostable, or unstable state for $L1_0$ were evaluated and tabulated.

7. ACKNOWLEDGMENTS

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