

Ordering and Phase Separation in FCC/L1₂ Alloys

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ABSTRACT

Over the past two decades investigations of alloys which undergo both atomic ordering and phase separation have been performed and published. Of import in such systems is the sequence of reactions which occur. Closely related to the sequence of reactions is the existence of and relative positions of instability curves. In thermodynamically first order disorder/order phase transformations, the following instability curves may exist: instability of the disordered phase to phase separation (T_S); instability of the disordered phase to atomic ordering (T_i); instability of the ordered phase to disordering (T_i^\dagger) and instability of the ordered phase to phase separation (T_{CS}). Various proposals concerning the configurations of these instability curves have been reported in the literature. In this paper we investigate the various possible configurations of the instability curves in a binary phase diagram with FCC and L1₂ as the possible phases by using the static concentration wave model developed by Khachatryan with two adjustable parameters: $V(0)$ and $V(\mathbf{k})$, where $\mathbf{k} = [100]$. By systematically varying the ratio of $V(0)$ to $V(\mathbf{k})$ we obtain five distinct configurations of the instability curves. The various configurations give rise to ten regions in which different reaction paths can be taken by the transforming supersaturated solid solution. These paths are discussed in detail. We compare our results with previous studies. *

* This work is based on the Ph.D. thesis of Jeffrey P. Simmons, which was sponsored in part by ALCOA Technical Center and the National Science Foundation (DMR 84-13115).

INTRODUCTION

One important phase transformation that occurs in the solid state is the formation of an ordered phase from a supersaturated solid solution. The overall reaction for this precipitation can be written as:



where α' is a supersaturated solid solution
 α is the solid solution in (meta)stable equilibrium with β
 β is the precipitate phase

In this paper we are interested in the case where α is FCC (Cu, $Fm\bar{3}m$, cF4)* and β is L1₂ (Cu₃Au, $Pm\bar{3}m$, cP4). For such systems there exist a myriad of reaction paths that can be followed in attaining equilibrium, depending on the overall alloy composition and reaction temperature.

Of particular interest to us in this paper is the occurrence of instability curves in the FCC/L1₂ phase diagram. It has been shown that the following instabilities exist in the first-order FCC/L1₂ system:^(1,2)

- (1) instability of FCC with respect to phase separation (T_s)
- (2) instability of FCC with respect to atomic ordering to L1₂ (T_i^-)
- (3) instability of L1₂ with respect to phase separation (T_{cs})
- (4) instability of L1₂ with respect to disordering (T_i^+)

The relative positions of these curves are of great importance in determining the possible sequence of reactions that occur at a given temperature. *A priori* we know $T_i^+ > T_i^-$ for a thermodynamic first order transition. However the position of T_s with respect to T_i^- and/or T_{cs} can not be determined without further information.

In his paper for this symposium Professor Cohen has reviewed the status of the *kinetics* of ordering and precipitation. Here we look at a related topic, namely the sequence of transitions which occur *due to instability*, that is, which occur with no barrier to transformation. Hence, our approach is not strictly time dependent (kinetics). However, unstable reactions usually occur faster at low temperature than nucleation reactions. Thus, our discussion will bear on the *sequence* of reactions that occur in materials that are far from equilibrium.

Below, we present the results we obtained when we modeled the FCC/L1₂ system by the static concentration wave technique proposed by Khachatryan. This model has two adjustable parameters: $V(0)$ and $V(100)$. $V(0)$ measures the tendency of the FCC phase to phase separate while $V(100)$ measures the tendency of the FCC phase to order to L1₂. Both of these are k space

* The structures are listed according to prototype, space group and Pearson symbol.

coefficients of the free energy. By systematically varying the ratio of $V(0)$ to $V(100)$ we obtain four distinct FCC/L1₂ instability diagrams. Importantly, these diagrams display ten distinct regions of instability. Herein we summarize our findings. In all cases we assume that atomic ordering processes occur much faster than phase separation. We refer the reader to the Ph.D. thesis of J. P. Simmons for the details of the model and calculations.⁽³⁾

Discussion

The equation for the free energy of the solid solution as a function of $V(0)$ and $V(100)$ has been derived by Khachatryan *et al.*⁽⁴⁾ as is shown below.

$$f = \frac{1}{2} (V(0)c^2 + 3V(100)\eta^2c^2) + \frac{1}{4} RT \left((1 - c(3\eta+1)) \ln(1-c(3\eta+1)) + c(3\eta+1) \ln c(3\eta+1) + 3c(1-\eta) \ln(3c(1-\eta)) + 3(1-c(1-\eta)) \ln(1-c(1-\eta)) \right). \quad (2)$$

By differentiating twice with respect to c and η respectively and setting the resultant equations equal to zero, the following two instability temperatures can be found:

$$T_s = - \frac{V(0)}{k} c(1 - c) \quad (3)$$

$$T_i = - \frac{V(100)}{k} c(1 - c) \quad (4)$$

These are inverted parabolic curves with maxima at $c = 0.5$.

We fix the value of $V(100)$ and vary $V(0)$ continuously. This produces different relative positions of each of the instabilities. Six different types of diagrams are obtained. The relative values of $V(0)$ and $V(100)$ which produce these diagrams are shown in Figure 1.

In sector (f) of Figure 1, both $V(0)$ and $V(100)$ are positive. Since neither spontaneous ordering or phase separation can occur, we will not discuss this situation.

When the values of $V(0)$ and $V(100)$ are negative and positive, respectively (i.e. sector (e)), the only instability is that of the FCC phase with respect to phase separation, T_s . The phase diagram with a miscibility gap is obtained. See Figure 2 which displays only the instability line, T_s . In region I of this diagram, the FCC phase is stable; in region X, the FCC phase is stable with respect to atomic ordering but unstable with respect to phase separation into two FCC disordered phases.

In sector (d) of Figure 1 the diagram with the relative positions of the instability curves shown in Figure 3 is produced. Here regions I and X are similar to those in Figure 2. But four other regions are formed, designated VIII, VI, VII and IX.

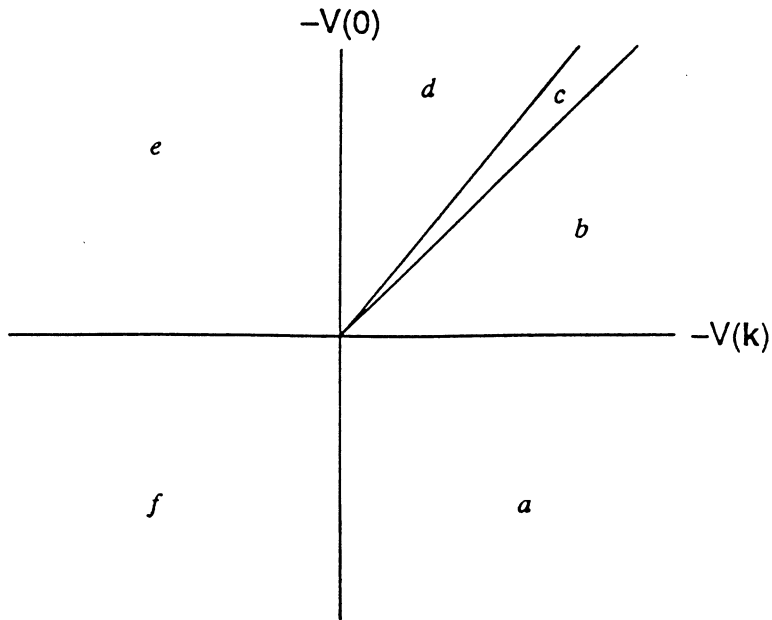


Figure 1. Diagram showing the different sectors whose $V(0)$ and $V(100)$ values produce the instability diagram shown in Figures 2-6.

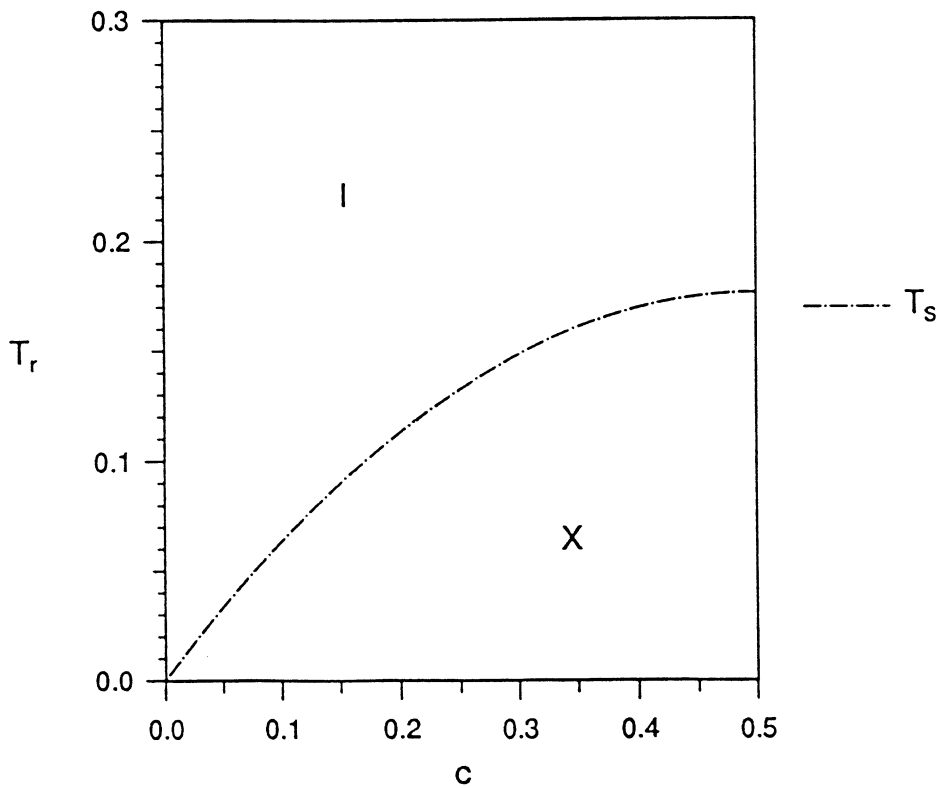


Figure 2. Instability Diagram from (e) of Figure 1 displaying only T_s .

In region VIII, the FCC phase is unstable with respect to phase separation and stable with respect to continuous atomic ordering. Therefore, an alloy quenched into this region would phase separate. After phase separation proceeds, the composition of the solute enriched region cuts across T_i^- into region VI. Here, the solute enriched regions become unstable with respect to atomic ordering and therefore develop long range order. This produces a two phase mixture (FCC and $L1_2$) which eventually reaches equilibrium.

In region VI, the FCC is unstable with respect to both phase separation and atomic ordering. We assume that the atomic ordering process proceeds much faster than the decomposition process, so the FCC phase orders to $L1_2$. The $L1_2$ phase thus formed is unstable with respect to decomposition into two ordered phases. The solute depleted ordered phase eventually cuts T_i^+ and becomes unstable with respect to disordering, giving rise to a two phase mixture (FCC + $L1_2$) that eventually reaches equilibrium.

In region VII of Figure 3, the FCC phase is unstable with respect to both decomposition and atomic ordering. As discussed above for region VI, we expect atomic ordering to occur first because of the kinetics. The ordered $L1_2$ single phase alloy thus formed is stable in region VII and does not evolve further by barrierless transition.

Finally an FCC phase quenched into region IX of Figure 3 is below T_s but above T_i^- . The FCC phase will decompose into two disordered phases until the solute enriched phase becomes unstable with respect to atomic ordering. It will order and again the two phases will eventually attain equilibrium.

When the $V(0)$ to $V(100)$ ratio puts the alloy in region (c) of Figure 1, the relative positions of the instability curves appear as shown in Figure 4. In this case only one new kind of region of instability is produced, namely the one designated as II. In this region the FCC phase is stable, since it is above both T_i^- and T_s . However if an ordered $L1_2$ phase is upquenched to a temperature in this region, it becomes unstable with respect to phase separation into two ordered regions. The solute depleted region eventually becomes unstable with respect to disordering eventually yielding a two phase FCC plus $L1_2$ mixture.

When the values of $V(0)$ to $V(100)$ are such that they are in region (b) of Figure 1, the instability lines appear as shown in Figure 5. In this diagram three new regions are obtained, namely III, IV and V.

In region III the FCC phase is stable with respect to the continuous formation of the ordered phase as well as stable with respect to phase decomposition. Therefore no barrierless reaction can occur. The ordered phase could form by a discontinuous, nucleation and growth type process, however.

In region IV, the FCC phase is unstable with respect to atomic ordering. Once the ordering occurs, the ordered alloy becomes unstable with respect to phase separation. This region is similar to VI, since in VI the instability of FCC with respect to decomposition is superseded by its instability with respect to ordering.

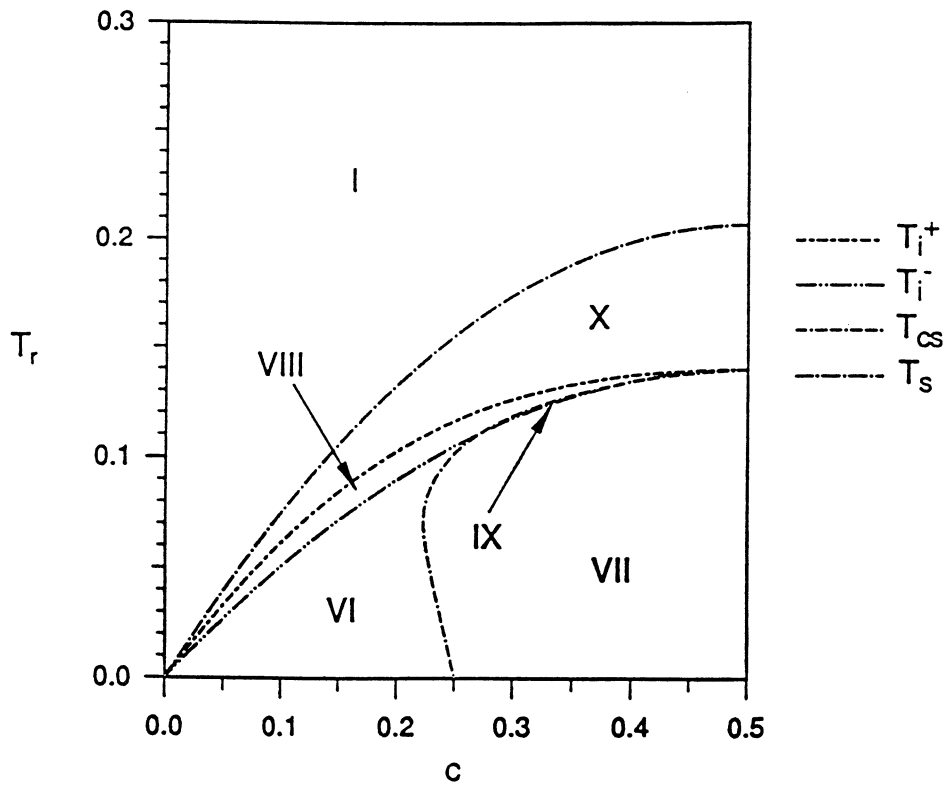


Figure 3. Instability diagram from (d) of Figure 1, displaying T_s , T_i^- , T_i^+ and T_{CS} . Here T_s is always greater than T_i^- . ($V(0)/k = -6000$; $V(100)/k = -4060$)

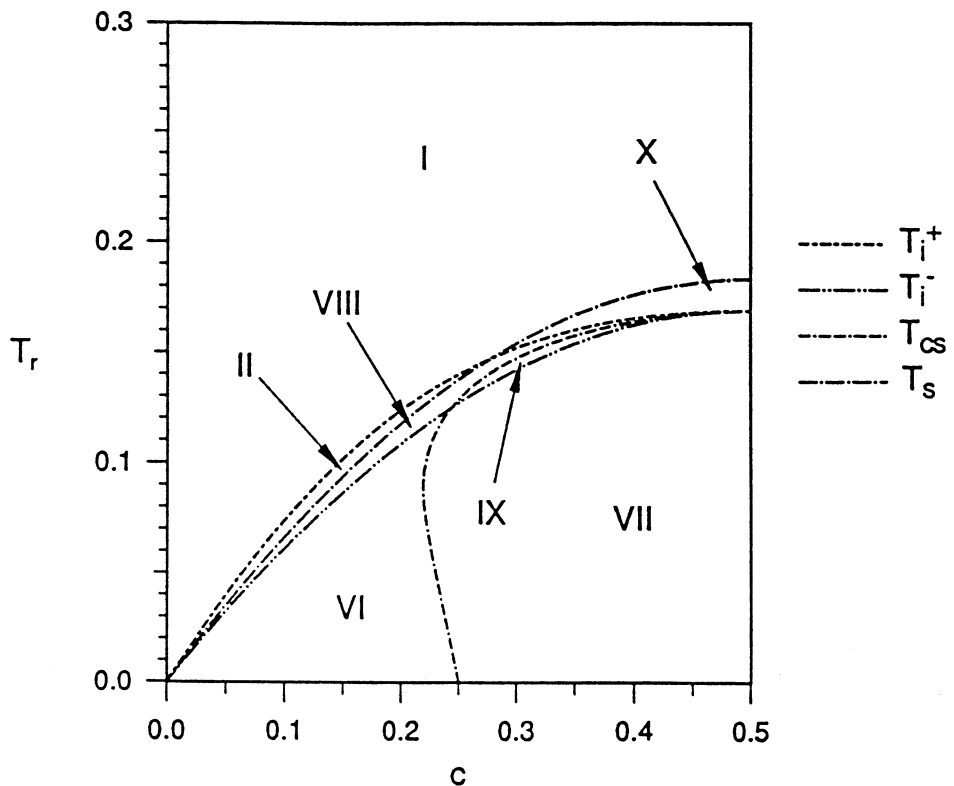


Figure 4. Instability diagram from region (c) of Figure 1. Here T_s cuts across T_i^+ . ($V(0)/k = -4400$; $V(100)/k = -4060$)

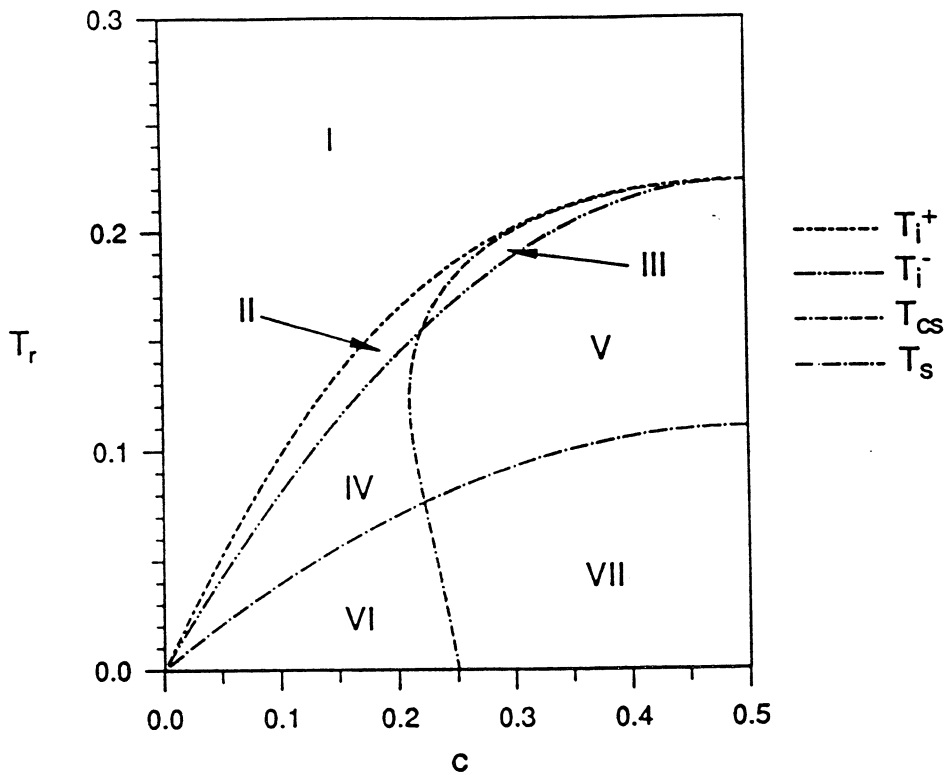


Figure 5. Instability diagram from region (b) of Figure 1. Here T_s is always less than T_i^- . ($V(0)/k = -2000$; $V(100)/k = -4060$)

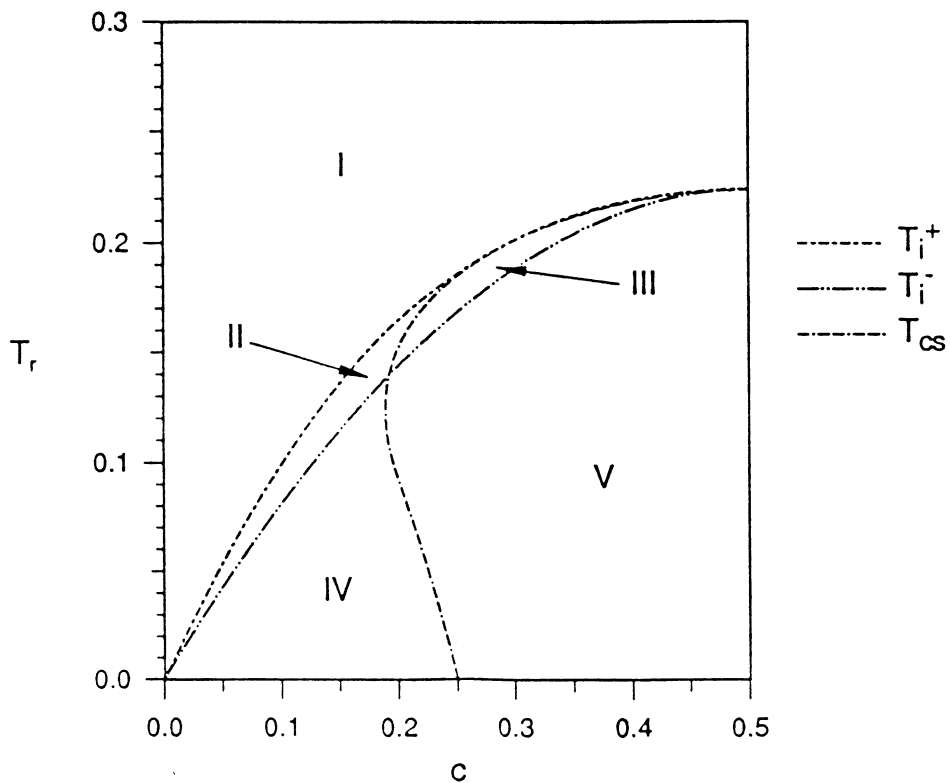


Figure 6. Instability diagram from region (a) of Figure 1. Here there is no possibility of the FCC phase being unstable with respect to phase separation. ($V(0)/k = -2000$; $V(100)/k = -4060$)

The reaction sequence in region V is like that of region VII for the same reason, namely the atomic ordering proceeds faster than phase separation.

Finally when $V(100) < 0$ and $V(0) > 0$ (region (a) of Figure 1), the FCC phase can only be unstable with respect to atomic ordering. No region of instability with respect to phase separation of the disordered phase exists. See Figure 6. Each of the regions in this diagram have been described above.

There are thus ten instability regions which occur in different configurations of the diagrams. Table 1 summarizes the instability diagrams, along with the ranges of $V(0)$ and $V(100)$, and displays which instability regions are found in each.

Table I

Sector	Range	Instability Regions
<i>a</i>	$V(\mathbf{k}) < 0, V(0) > 0$	I, II, III, IV, V
<i>b</i>	$V(\mathbf{k}) < 0, V(0)/V(\mathbf{k}) < 1$	I, II, III, IV, V, VI, VII
<i>c</i>	$V(\mathbf{k}) < 0, 1 < V(0)/V(\mathbf{k}) < 1.243$	I, II, VI, VII, VIII, IX, X
<i>d</i>	$V(\mathbf{k}) < 0, 1.243 < V(0)/V(\mathbf{k})$	I, VI, VII, VIII, IX, X
<i>e</i>	$V(\mathbf{k}) > 0, V(0) < 0$	I, X
<i>f</i>	$V(\mathbf{k}) > 0, V(0) > 0$	I

It is interesting to note that each of these regions of stability have been predicted by Soffa and Laughlin using a qualitative graphical thermodynamics approach.⁽²⁾ Also, Kulbarni *et al.*⁽⁷⁾ have used pairwise interaction parameters to study the relative position of the instability curves in such systems. Their model is implicitly one of a second order transition. Thus they have not included an instability curve for the ordered phase with respect to disordering.

The instability diagram shown in Figure 6 is essentially that obtained by Khachatryan *et al.*⁽⁴⁾ in their modeling of Al-Li, as the values of $V(0)$ and $V(100)$ used to produce it were similar to the values that Khachatryan *et al.* calculated for Al-Li. In this diagram, no FCC instability with respect to phase separation exists. As pointed out by Khachatryan *et al.*⁽⁴⁾ the FCC phase is only unstable with respect to atomic ordering for these values of $V(0)$ and $V(100)$. As discussed above, once the FCC phase orders to $L1_2$, the $L1_2$ phase can become unstable with respect to phase separation if the temperature and composition are in region IV of the diagram. Khachatryan *et al.* call this sequence of reactions a *cascade of instabilities*. This concept is like the "conditional spinodal" defined by Allen and Cahn⁽⁵⁾ in higher order order/disorder phase diagrams, in that the decomposition process is contingent on prior ordering.

Sigli and Sanchez,⁽⁶⁾ on the other hand, have modeled the Al-Li phase diagram by the cluster variation technique. Their approach a predicted region of instability of FCC with respect to phase decomposition (*viz.* a metastable miscibility gap or FCC). Their diagram is similar to Figure 5, shown above.

It is very difficult to determine experimentally which of these diagrams is "correct". If the FCC phase is quenched into region VI of Figure 5, the sequence of reactions would be identical to the ones occurring in region IV of the diagram, since the atomic ordering process proceeds much faster than the phase separation one. Hence, it may be impossible to distinguish experimentally between these two diagrams, by merely documenting the reaction sequences.

SUMMARY

Using the static concentration wave model we have demonstrated that ten possible regions of instability can exist in FCC/L₁₂ phase diagrams. Within each of these regions, distinct reaction behavior is predicted to occur. These reaction sequences have been discussed, region by region. We find that there are four distinct configurations of instability lines in the static concentration wave model. The "instability diagrams" so produced were compared to predictions of other workers.

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ACKNOWLEDGEMENTS

We wish to thank the organizers of this symposium for inviting us to participate. Also we wish to thank Jerry Cohen for his many important and carefully performed experimental papers on materials research. We join with the others in wishing him continued success.