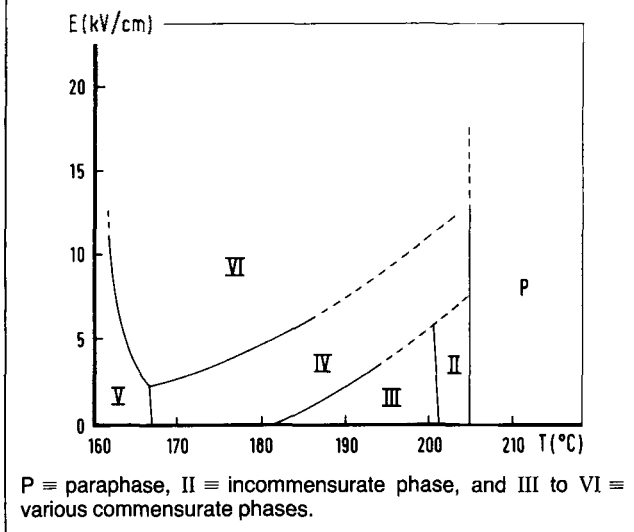


**Fig. 7 Electric Field vs Temperature Phase Diagram of RbLiSO<sub>4</sub>, [Ref 12]**



## Concluding Remarks

In several materials, phases occur that are not crystallographic in the usual sense. These incommensurate phases may be understood as the consequence of the presence of more than one ordering mechanism that favor different periodicities. A simple model that takes into account inter-

action with first, second, and third neighbors shows the main features of many materials with incommensurate phases. Moreover, the essential role played by the non-linearity causes a wealth of unexpected and interesting phenomena, which include intermediate incommensurate phases, discommensurations, and chaotic states. Also, the physical properties of these materials are uncommon. For the interested reader, we refer to Ref 13 and 14.

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# Phase Diagram Features Associated with Multicritical Points in Alloy Systems\*

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Many features in the vicinity of critical points in phase diagrams can be illustrated using a Landau-type free energy expansion as a power series in one or more order parameters and composition. This simple approach can be used with any solution model. It also predicts limits to metastability and is useful for understanding mechanisms of phase change. The theory is applied to all the critical points that can occur in binary systems according to a Landau theory: critical consolute points, order-disorder transitions, tricritical points, critical end points, as well as systems in which two transitions such as chemical and magnetic ordering occur.

Higher-order phase transitions are common features of alloy phase diagrams. At first-order phase transitions, quite different phases with differing structures, order parameters, compositions, enthalpies, entropies, and/or densities coexist at equilibrium. In contrast, at a higher-order phase transition several phases, and domains within

some of the phases, become identical in every respect. As a result there are no discontinuities in composition, entropy, and molar volume and, therefore, the free energy

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and its first derivatives are continuous at the transition. Nonetheless, these transitions are characterized by singularities in the thermodynamic functions that in phase diagrams occur at critical points or along critical lines or surfaces.

A major goal of the study of critical phenomena is to derive a detailed description for the thermodynamic behavior, especially the singularities, and to account for the large variety of possible critical points, many of which are found in alloy systems. The celebrated renormalization group approach has made dramatic breakthroughs possible.<sup>1,2</sup> However, an older simpler approach due to Landau<sup>3</sup> is both realistic for solid systems and consistent with the kinds of models commonly used in alloy phase diagram calculations.

In the absence of long-range interactions, fluctuations dominate critical behavior and result in singularities that are characterized by irrational exponents in the temperature and composition dependence of thermodynamic properties in the critical region. In solids, atomic size differences give rise to long-range elastic interactions that can reduce the fluctuations to a point where classical rational exponents are expected.<sup>4,5</sup> Most solution models implicitly do not allow for fluctuations and give rise to analytic free energy expressions except at critical points and curves, and even then the exponents are rational.

In the critical region the various phases and domains differ little from one another, and all approach the common critical phase in every respect as the critical point is approached. Because of this, a single theoretical model may be used to describe both the critical phase and the various phases and domains near the critical point. Landau's approach was to use a single free energy function that is a power series in variables that express distance from the critical point. It is compatible with all solution models that give rise to an analytic free energy expression, because these can always be expressed as a Taylor's expansion. In this sense, Landau's approach is model independent. It leads to a remarkably simple understanding of how the singularities arise and gives detailed descriptions about thermodynamic behavior. It necessarily gives classical rational exponents and, because of this, is limited to those solid systems in which fluctuations do not become so dominant that irrational exponents are expected.

Using the Landau theory, the phase diagram features of all of the critical points in binary alloy systems are developed. Where a miscibility gap between phases of identical structure narrows to a point, a consolute point is seen, e.g., in Au-Ni.<sup>6</sup> In  $\beta$  Cu-Zn,<sup>7</sup> the long-range order parameter disappears along a locus of points of higher-order transitions where the disordered phase and two ordered domains become identical. A tricritical point occurs where a line of higher-order transitions merges with a two-phase field of the same two phases.<sup>8</sup> Two order parameters are involved in bicritical and tetracritical points.<sup>8</sup> At a bicritical point, three phases meet, separated by two lines of higher-order transitions and a two-phase field. At a tetracritical point, four phases meet, separated by four lines of higher-order transitions. Higher critical points than tetracritical cannot occur in a binary system with pressure fixed.

The Fe-Si phase diagram contains a tricritical point at 13 at.% Si and a tetracritical point where a line of Curie points crosses a line of order-disorder transitions.<sup>9</sup> There are multicritical points in both the coherent and incoher-

ent Fe-Al phase diagrams<sup>10,11</sup> at the point where a line of higher-order transitions ends at miscibility gap. We believe that in the incoherent diagram, there is a bicritical point where a line of Curie points intersects the line of order-disorder transitions. The miscibility gap must begin at a lower temperature in the coherent diagram, and this point is thus a tricritical point.

## Preliminaries

### Thermodynamic Variables

For the sake of simplicity, only binary alloys at constant pressure will be considered. Values of the usual state variables, temperature,  $T$ , and average composition,  $c$ , for such a system fix the free energy. For systems with critical points, it is often necessary to consider as well the existence of other variables, generally called *order parameters*, which at equilibrium assume values that depend on  $T$  and  $c$ . For example, in ordered  $\beta$  brass, an order parameter could be defined as the difference between average compositions on the Cu and Zn sublattices. In contrast to composition variables, order parameters are not conserved quantities. They are "hidden" variables in the sense that they are neither consciously controlled nor associated with an extra thermodynamic degree of freedom in the system. They do, however, adopt equilibrium values associated with extrema of free energy. Order parameters play a key role in the thermodynamics of phase transitions near critical points.

The free energy,  $F$ , for a binary system at constant pressure with critical points is, therefore, expressed most generally as a function of  $T$ ,  $c$ , and one or more order parameters. For binaries, no more than two order parameters, denoted by  $\eta$  and  $\nu$ , need to be considered and thus:

$$F = F(T, c, \eta, \nu) \quad (\text{Eq 1})$$

The function  $F$  is assumed to be a "coarse grained" free energy; that is, the free energy of a system in which *local* averages of composition and order parameters are constrained to be constant.<sup>12</sup>

### Equilibrium Conditions

Equilibrium values of order parameters  $\eta$  and  $\nu$  are determined from the conditions:

$$\partial F / \partial \eta = 0 \quad \text{and} \quad \partial F / \partial \nu = 0 \quad (\text{Eq 2})$$

The necessary condition for stability of the equilibrium state with respect to variations of order parameter is that the matrix of second derivatives of  $F$  with respect to the order parameters be positive definite. Stable equilibrium values of the order parameters define loci  $\eta_e(T, c)$  and  $\nu_e(T, c)$ . The free energy,  $F_e$ , of a system with equilibrium values of the "hidden" variables  $\eta$  and  $\nu$  can then be expressed as:

$$F_e = F[T, c, \eta_e(T, c), \nu_e(T, c)] = F_e(T, c) \quad (\text{Eq 3})$$

In Eq 3,  $\eta_e$  and  $\nu_e$  take on the role of intermediate variables between the dependent variable,  $F_e$ , and independent variables,  $T$  and  $c$ .

For stability of the system with respect to variations of composition, it is necessary that the second derivative of  $F_e$  with respect to composition be positive. When multiphase equilibrium states are stable, coexisting compositions  $c_a$

and  $c_\beta$  between phase  $\alpha$  and  $\beta$  are found from the "common tangent" conditions:

$$\left. \frac{\partial F_\alpha}{\partial c} \right|_{c_\alpha} = \left. \frac{\partial F_\beta}{\partial c} \right|_{c_\beta} \quad (\text{Eq 4})$$

and

$$\frac{F_\alpha(c_\alpha) - F_\beta(c_\beta)}{c_\alpha - c_\beta} = \left. \frac{\partial F_\alpha}{\partial c} \right|_{c_\alpha} \quad (\text{Eq 5})$$

where  $F_\alpha$  and  $F_\beta$  are the equilibrium ( $F_e$ ) free energy functions for phases  $\alpha$  and  $\beta$ , respectively.

### The Landau Expansion and Phase Transitions

The free energy function used in the Landau model of phase transitions has the form of an expansion of  $F$  into a power series about the critical point. For such an expansion to be valid,  $F$  must have continuous derivatives of all orders. Therefore, the strict validity of the Landau model hinges on whether or not  $F$  is analytic at the critical point.

Phase transitions are located at singularities in free energy. One may well ask how singularities arise from an assumed analytic  $F$  to give phase transitions in this model. The apparent contradiction is eliminated when the hidden variables, the order parameters, and the possibility of separation into phases differing in composition are properly accounted for. It is the function  $F_e$ , rather than  $F$ , that characterizes equilibrium, and which must be examined to locate and classify phase transitions.

### Consolute Points

The locus of temperatures,  $T_s(c)$ , where  $F_{cc} = 0$ , called the spinodal, is the boundary of a region in which a homogeneous solution is unstable. The slope of the spinodal is given by  $dT_s/dc = -F_{ccc}/F_{ccT}$ , where the subscripts denote partial differentiation. Extreme values of  $T_s$  give rise to a type of critical point known as a consolute point, where two coexisting phases become identical and the miscibility gap vanishes. The condition for such a point is given by two equations:  $F_{cc} = 0$ , and either  $dT_s/dc = 0$  or  $F_{ccc} = 0$ .

A Landau-type expansion of  $F(T, c)$  about the critical point ( $T_c, c_c$ ) may be used to obtain quantitative relationships for phase equilibria near consolute points.<sup>13</sup> Retaining a minimum number of terms necessary to make the model realistic in the limit of approach to the critical point,  $F$  is expressed:

$$F = F^0 + F_c(c - c_c) + \frac{1}{24}F_{cccc}(c - c_c)^4 + F_T(T - T_c) + \frac{1}{2}F_{TT}(T - T_c)^2 + F_{cT}(T - T_c)(c - c_c) + \frac{1}{2}F_{ccT}(T - T_c)(c - c_c)^2 \quad (\text{Eq 6})$$

where the subscripts on  $F$  denote partial differentiation. The derivatives are to be evaluated at the critical point. Second and third powers of  $(c - c_c)$  are absent from Eq 6 because the coefficients  $F_{cc}$  and  $F_{ccc}$  are zero.

**Coexistence Curves.** Coexisting compositions are found by substituting the expression for  $F$  into Eq 4 and 5. The only terms that contribute to the calculations are those

with coefficients  $F_{cccc}$  and  $F_{ccT}$ . Because these terms are symmetric about  $c = c_c$ , the equilibrium compositions  $c_\alpha$  and  $c_\beta$  will be equidistant from  $c_c$ , and the volume fractions of the phases will be equal. Cook and Hilliard define:

$$\Delta c_e = c_\beta - c_c = c_c - c_\alpha$$

When  $F_{ccT}(T - T_c)$  is negative, the equilibrium condition becomes:

$$F_{cccc}(\Delta c_e)^2 + 6F_{ccT}(T - T_c) = 0$$

with the result:

$$\Delta c_e = \pm \left[ \frac{6F_{ccT}(T_c - T)}{F_{cccc}} \right]^{1/2} \quad (\text{Eq 7})$$

To demonstrate that there is a transition at the consolute point, expressions for  $F$  and its derivatives are required along the equilibrium path of approach to the critical point. For the single-phase equilibrium state with  $c = c_c$ ,  $F_e$  is given from Eq 6 as:

$$F_e = F^0 + F_T(T - T_c) + \frac{1}{2}F_{TT}(T - T_c)^2 \quad (\text{Eq 8})$$

For the two-phase equilibrium state, an expression for the free energy,  $F_e$ , of a mixture of phases with average composition  $c = c_c$  and with phase compositions following the coexistence curves is obtained by combining Eq 6 and 7 giving an expression having the functional form:

$$F_e = F[T, \Delta c_e(T)] \quad (\text{Eq 9})$$

The equation for the free energy of the equilibrium two-phase state is:

$$F_e = F^0 + F_T(T - T_c) + \frac{1}{2} \left[ F_{TT} - \frac{3(F_{ccT})^2}{F_{cccc}} \right] (T - T_c)^2 \quad (\text{Eq 10})$$

Because of the particularly simple functional form of Eq 6 and 7, the intermediate variable  $\Delta c_e$  has been eliminated in Eq 10. Differentiation of Eq 8 and 10 can therefore be carried out directly and demonstrates that the second derivatives of  $F$  change discontinuously at the consolute point. The transition is second order.

**Spinodals.** The spinodals, which are the loci of  $\partial^2 F / \partial c^2 = 0$ , can be computed by differentiating Eq 6. The spinodals are also symmetric about  $c = c_c$  in this model. Defining  $c_s$  to be the composition of the spinodal, and:

$$\Delta c_s = c_s - c_c$$

it is easily shown that:

$$\Delta c_s = \pm \left[ \frac{2F_{ccT}(T_c - T)}{F_{cccc}} \right]^{1/2} \quad (\text{Eq 11})$$

Equations 7 and 11 show that, sufficiently close to the consolute point, both the spinodals and the coexistence curves are parabolic. We note also that the ratio  $\Delta c_s / \Delta c_e$  is equal to  $\sqrt{3}$ , as shown originally by Cook and Hilliard.<sup>13</sup> When fluctuations dominate and result in irrational exponents, the spinodal is much closer to the phase boundary. Instead of  $\sqrt{3}$ , Gaunt and Baker<sup>14</sup> estimate 1.18.

### Order-Disorder Transitions at Fixed Composition

In this section, the Landau model is used to describe the free energy of phases that undergo order-disorder transitions which are associated, for instance, with the ordering of magnetic spins or of atoms on a lattice. Landau recognized that such transitions could be either first-order or higher-order, and developed, based on the symmetries of the phases, a set of necessary (but not sufficient) conditions for a transition to be higher-order.<sup>8</sup> Both types can be modeled from a free energy expansion in powers of a single-order parameter.

The order parameter  $\eta$  is defined to be a measure of the deviation from an equilibrium (stable, metastable, or unstable) state that is called disordered and for which we set  $\eta = 0$ . In the Landau model,  $F$  is written as a power series in  $\eta$ :

$$F = F^0 + \frac{1}{2}F_{\eta\eta}\eta^2 + \frac{1}{6}F_{\eta\eta\eta}\eta^3 + \frac{1}{24}F_{\eta\eta\eta\eta}\eta^4 \quad (\text{Eq 12})$$

where  $F^0$  and the derivatives of  $F$  are functions of  $T$  and  $c$ , and the derivatives are evaluated at  $\eta = 0$ . To avoid minima at large values of  $\eta$ , it is necessary that  $F_{\eta\eta\eta\eta}$  be positive.

**First-Order Transition.** Equation 12 is plotted schematically for different relative values of  $F_{\eta\eta}$ ,  $F_{\eta\eta\eta}$ , and  $F_{\eta\eta\eta\eta}$  in Fig. 1. The curves reflect the variation of  $F$  with temperature for a first-order transition between the ordered and disordered states. Equilibrium values of the order parameter are obtained by substituting Eq 12 into Eq 2, giving:

$$\eta \left( F_{\eta\eta} + \frac{1}{2}F_{\eta\eta\eta}\eta + \frac{1}{6}F_{\eta\eta\eta\eta}\eta^2 \right) = 0$$

Thus,  $\eta = 0$  is an extremum of  $F$  as well as  $\eta = \eta_e$ , where  $\eta_e$  is a root to the equation:

$$F_{\eta\eta} + \frac{1}{2}F_{\eta\eta\eta}\eta_e + \frac{1}{6}F_{\eta\eta\eta\eta}(\eta_e)^2 = 0 \quad (\text{Eq 13})$$

The order-disorder transition occurs at a temperature,  $T_0$ , where the free energy of the disordered state  $\eta = 0$  and the ordered state with equilibrium order parameter  $\eta_e(T_0)$  are equal, as depicted in Fig. 1(c). That is:

$$F^0 = F^0 + \frac{1}{2}F_{\eta\eta}(\eta_e)^2 + \frac{1}{6}F_{\eta\eta\eta}(\eta_e)^3 + \frac{1}{24}F_{\eta\eta\eta\eta}(\eta_e)^4 \quad (\text{Eq 14})$$

Equations 13 and 14 are both satisfied for the conditions:

$$F_{\eta\eta} = (F_{\eta\eta\eta})^2 / 3F_{\eta\eta\eta\eta} \quad (T = T_0) \quad (\text{Eq 15})$$

and

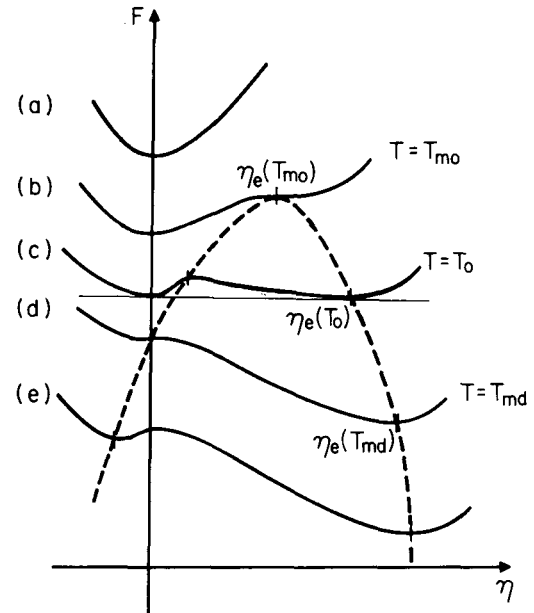
$$\eta_e(T_0) = -2F_{\eta\eta\eta} / F_{\eta\eta\eta\eta} \quad (\text{Eq 16})$$

Two other free energy curves in Fig. 1 are of special interest. Curves (b) and (d) depict the free energy curves at the limits to metastability of the ordered and disordered phases, respectively. The limit to metastability of the ordered phase occurs at a temperature denoted by  $T_{mo}$ , at which the discriminant in Eq 13 is zero, i.e.:

$$F_{\eta\eta} = 3F_{\eta\eta\eta}^2 / 8F_{\eta\eta\eta\eta} \quad (T = T_{mo}) \quad (\text{Eq 17})$$

and at the value of  $\eta_e$  given by:

Fig. 1 First-Order Transitions



When  $F$  is asymmetric about  $\eta = 0$ , higher-order transitions cannot occur. Metastability characteristic of first-order transitions terminates at  $T_{mo}$  and  $T_{md}$ . Extrema of  $F$  are at  $\eta = 0$  and along the dashed parabola.

$$\eta_e(T_{mo}) = -3F_{\eta\eta\eta} / 2F_{\eta\eta\eta\eta} \quad (\text{Eq 18})$$

The limit to metastability of the disordered phase occurs at the temperature  $T_{md}$ , where the smaller root to Eq 13 is zero.  $T_{md}$  is, thus, the temperature at which:

$$F_{\eta\eta} = 0 \quad (T = T_{md}) \quad (\text{Eq 19})$$

The order-disorder transformation at the equilibrium temperature,  $T_0$ , is easily shown to be first order for all values of  $F_{\eta\eta\eta}$  except zero, by using Eq 12 and 16 to calculate the value of  $dF_e/dT$  in the limit  $T \rightarrow T_0$ .

**Second-Order Transition.** According to Landau,<sup>3</sup> when symmetry principles dictate that crystal properties are expressible as even functions of the order parameter, the coefficient  $F_{\eta\eta\eta}$  in Eq 12 is identically zero, and second-order transitions can occur. The free energy expansion becomes:

$$F = F^0 + \frac{1}{2}F_{\eta\eta}\eta^2 + \frac{1}{24}F_{\eta\eta\eta\eta}\eta^4 \quad (\text{Eq 20})$$

Again,  $F_{\eta\eta\eta\eta}$  is assumed positive. The equilibrium order parameter,  $\eta_e$ , is found from Eq 2 to be a root to the equation:

$$\eta_e \left[ F_{\eta\eta} + \frac{1}{6}F_{\eta\eta\eta\eta}(\eta_e)^2 \right] = 0 \quad (\text{Eq 21})$$

For  $F_{\eta\eta}$  is positive,  $\eta_e = 0$  is the only root to Eq 21, and the disordered phase is the minimum free energy state. When  $F_{\eta\eta}$  is negative,  $\eta = 0$  is a local maximum of  $F$ , and two additional real roots to Eq 21 exist that give absolute minima of  $F$ . These are:

$$\eta_e = \pm (-6F_{\eta\eta} / F_{\eta\eta\eta\eta})^{1/2} \quad (\text{Eq 22})$$

The equilibrium ordered state thus consists of coexisting "domains" with order parameters that are equal in magnitude, but opposite in sign. These domains exist in alloys and are separated by interfaces called antiphase boundaries or magnetic domain walls.

The transition from ordered to disordered equilibrium states in the free energy model for second-order transition thus occurs when  $F_{\eta\eta}$  changes sign. The locus of order-disorder transitions in a phase diagram is, therefore, given by:

$$F_{\eta\eta}(T, c) = 0 \quad (\text{Eq 23})$$

From the properties of derivatives, we can express the slope of the order-disorder transition in a temperature-composition diagram as:

$$-dT/dc = F_{\eta\eta c}/F_{\eta\eta T} \quad (\text{Eq 24})$$

The order of the transition is most straightforwardly assessed by direct substitution of Eq 22 into Eq 20 to give the following expressions for  $F_e$ :

$$F_e = \begin{cases} F^0 & (F_{\eta\eta} \text{ positive}) \\ \Phi & (F_{\eta\eta} \text{ negative}) \end{cases} \quad (\text{Eq 25})$$

where

$$\Phi \equiv F^0 - 3(F_{\eta\eta})^2/2F_{\eta\eta\eta\eta} \quad (\text{Eq 26})$$

Because the functional form of  $F_e$  is different for the two phases, it will be convenient to use the symbols  $F^0$  and  $\Phi$  for the specific phases and  $F_e$  in general for either or both phases.

In the limit as  $F_{\eta\eta} \rightarrow 0$ ,  $\partial\Phi/\partial c = \partial F^0/\partial c$ , but:

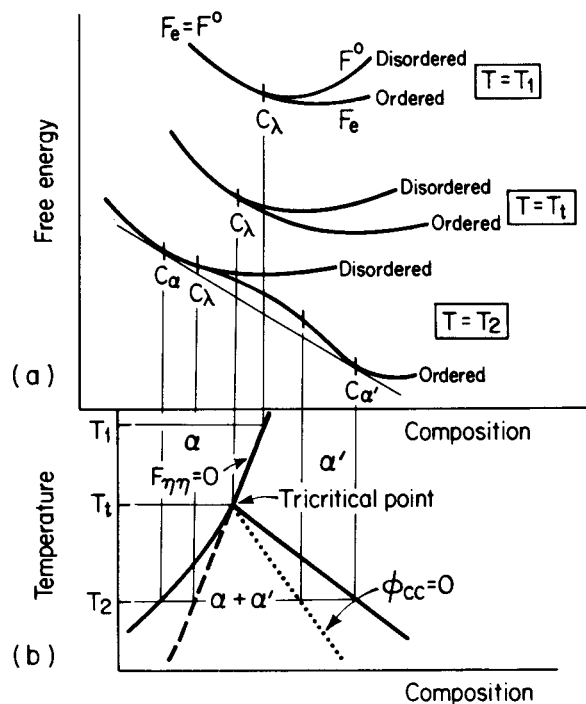
$$\Phi_{cc} = \partial^2 F^0/\partial c^2 - 3(F_{\eta\eta c})^2/F_{\eta\eta\eta\eta} \quad (\text{Eq 27})$$

Thus,  $\partial F_e/\partial c$  is continuous, but  $\partial^2 F_e/\partial c^2$  has a discontinuity. The transition is second order and the curvature of  $F_e$  is discontinuously lowered in the ordered phase at the transition.

When  $F_{\eta\eta\eta}$  is not required to be identically zero by symmetry, a second-order transition can nonetheless occur<sup>3</sup> at the point of intersection if any of the curves  $F_{\eta\eta} = 0$  and  $F_{\eta\eta\eta} = 0$ . This critical point is topologically analogous to a eutectic, except that all three phases have become identical. Three two-phase coexistence fields radiate from this point. Each is similar to the two-phase field of Fig. 2. One of the phases is disordered, the other two differ in the sign of  $\eta$ , which in this instance gives phases no longer identical by symmetry. Under some conditions more than three phases can meet at such a point. To the best of our knowledge, no such critical point has ever been reported. An early theory of order-disorder in face-centered cubic crystals gave such a point with four coexisting phases.<sup>15</sup>

**Tricritical Points.** In the previous section, order-disorder transitions at constant composition were examined. Stability with respect to variations in composition requires that  $\partial^2 F_e/\partial c^2$  be positive. Near an order-disorder transition, this condition will fail for the ordered phase before it will fail for the disordered phase. In this section, the point along an order-disorder transition, where the ordered phase is about to become unstable with respect to composition variations, will be examined. Such a point is a

**Fig. 2 Relationships Between Schematic Free Energy Curves and a Phase Diagram Containing a Tricritical Point**



(a) To the right of  $c_\lambda$ ,  $F_e$  diverges from  $F^0$  with a discontinuously lower curvature. Below  $T_t$ ,  $F_e$  has a region of negative curvature. (b) The tricritical point occurs at the intersection of  $F_{\eta\eta} = 0$  and  $\Phi_{cc} = 0$ , if  $\Phi_{ccc}/F_{\eta\eta c}$  is negative. One coexistence curve is tangent to the locus  $F_{\eta\eta} = 0$ , the other is not.

candidate for being a tricritical point and is given by the two conditions:

$$F_{\eta\eta} = 0 \quad (\text{Eq 28a})$$

and

$$\Phi_{cc} = 0 \quad (\text{Eq 28b})$$

Figure 2 illustrates the relationships between schematic free energy curves and a temperature-composition diagram for temperatures greater than, equal to, and less than the tricritical temperature,  $T_t$ . A second-order transition between phases  $\alpha$  and  $\alpha'$  and its metastable extension into the miscibility gap are illustrated. At each temperature, the composition of the transition is denoted by  $c_\lambda$ .  $\Phi_{cc}$  is the curvature of the free energy for the ordered phase. For  $T$  greater than  $T_t$ ,  $\Phi_{cc}$  is positive at  $c_\lambda$ . For  $T = T_t$ ,  $\Phi_{cc} = 0$  at  $c_\lambda$ . And for  $T$  less than  $T_t$ ,  $\Phi_{cc}$  is negative over a range of compositions from  $c_\lambda$  to  $c_s$ . The dotted curve on the phase diagram represents the locus  $\Phi_{cc} = 0$ . It is a spinodal curve that defines the limit to metastability of the ordered phase with equilibrium order parameter. The other boundary to the region, in which  $\Phi_{cc}$  is negative, is the metastable extension of the line order-disorder transitions. The regions for which  $\Phi_{cc}$  is negative has been called a *conditional spinodal* because the instability can only be realized if the system is ordered.<sup>16</sup>

**Coexistence Curves.** For deriving the functional form of the coexistence curves in the vicinity of the tricritical point, the algebra is greatly simplified if the expansion is done about the composition  $c_\lambda$ . Details will not be given here. The general method involves using separate free energy expansions for ordered and disordered phases, then using Eq 4 and 5 to solve for the equilibrium compositions. Quadratic terms in  $(c - c_\lambda)$  are required for the free energy expansion for the disordered phase, and both quadratic and cubic terms are required for the ordered phase. Representing the coexisting compositions by  $c_{\alpha'}$  and  $c_\alpha$  for the ordered and disordered phases, respectively, the functional relationships obtained are:

$$c_{\alpha'} - c_\lambda = -(3\Phi_{ccT}/2\Phi_{ccc})(T - T_t) \quad (\text{Eq 29})$$

and

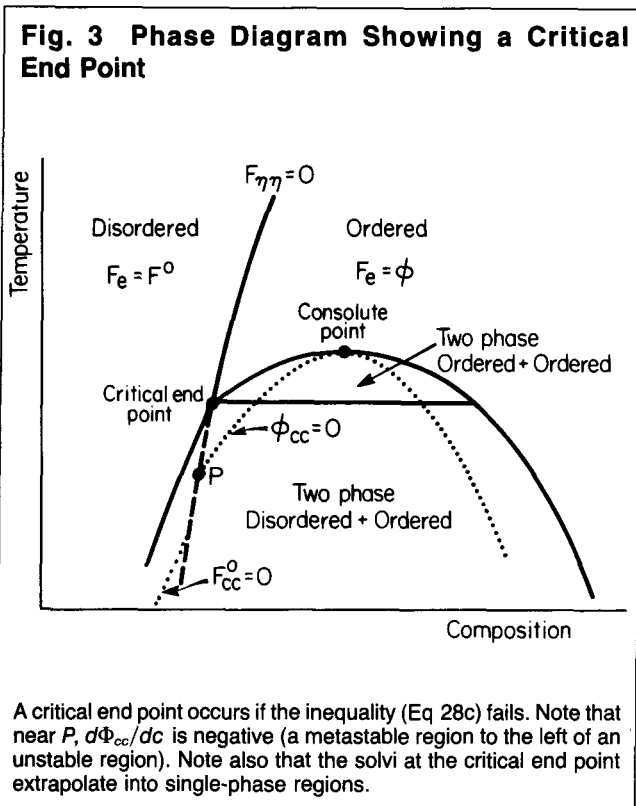
$$c_\alpha - c_\lambda = -[3(\Phi_{ccT})^2/8\Phi_{ccc}F_{cc}](T - T_t)^2 \quad (\text{Eq 30})$$

The phase diagram in Fig. 2 is drawn to reflect these functional dependencies.

### Critical End Points

Both conditions in Eq 28 are satisfied at the point  $P$  in another type of phase diagram, Fig. 3, in which the spinodal associated with a consolute point intersects the critical ordering transition curve deep within the miscibility gap. The point of intersection of the critical curve with the solvus is called a critical end point. For a tricritical point rather than a critical end point to appear, an additional condition is necessary:

$$\Phi_{ccc}/F_{\eta\eta c} < 0 \quad (\text{Eq 28c})$$



If Eq 28(c) fails, the point  $P$  appears within a two-phase region.

The changes of slopes of the solubility curves of the two phases above and below the critical end point are obtained from an examination of the factors in the Gibbs-Konovalev equation.<sup>17</sup> Because  $\partial^2 F/\partial c^2$  changes discontinuously, the left hand curve in Fig. 3 has a discontinuous change of slope with the slope of the disordered solvus steeper than for the ordered solvus. No change in the sign of the slope is permitted. It should be noted that the phase diagram lines at a critical end point can extrapolate into single-phase regions. The right-hand solvus is smoothly curved through the critical end point temperature.

### Bicritical and Tetracritical Points

The intersection of two lines of higher-order transitions gives rise to the possibility of a point of four-phase coexistence: disordered phase I ( $\eta = 0, \nu = 0$ ); two singly ordered phases, II ( $\eta = 0, \nu \neq 0$ ) and III ( $\eta \neq 0, \nu = 0$ ); and a phase IV, in which both order parameters take on nonzero values. Figure 4 illustrates these transitions on a temperature-composition diagram. Instead of Eq 20, a free energy expansion in even powers of both  $\eta$  and  $\nu$  is given as:

$$F = F^0 + \frac{1}{2}F_{\eta\eta}\eta^2 + \frac{1}{2}F_{\nu\nu}\nu^2 + \frac{1}{4}F_{\eta\eta\nu\nu}\eta^2\nu^2 + \frac{1}{24}F_{\eta\eta\eta\eta}\eta^4 + \frac{1}{24}F_{\nu\nu\nu\nu}\nu^4 \quad (\text{Eq 31})$$

The intersection occurs at  $F_{\eta\eta} = 0, F_{\nu\nu} = 0$ . Let us follow the critical curve between phases I and III. For this we have  $F_{\eta\eta} = 0, F_{\nu\nu}$  positive. Beyond this transition for phase III we have  $\eta_e^2 = -6F_{\eta\eta}/F_{\eta\eta\eta}$  and Eq 26 can be written for  $\Phi$ . However, the  $\nu$ -terms should be kept and written:

$$\Phi(\eta_e) = \left[ F^0 - \frac{3(F_{\eta\eta})^2}{2F_{\eta\eta\eta}} \right] + \frac{1}{2} \left[ F_{\nu\nu} - \frac{3F_{\eta\eta}F_{\eta\eta\nu\nu}}{F_{\eta\eta\eta}} \right] \nu^2 + \frac{1}{24}F_{\nu\nu\nu\nu}\nu^4 \quad (\text{Eq 32})$$

where the notation  $\Phi(\eta_e)$  indicates that the  $\eta_e$  value has been substituted. This is a Landau expansion in  $\nu$ , valid whenever  $\eta_e$  differs from zero. As long as  $\Phi(\eta_e)_{\nu\nu}$  is positive,  $\nu_e = 0$  and we have Eq 26. However, when:

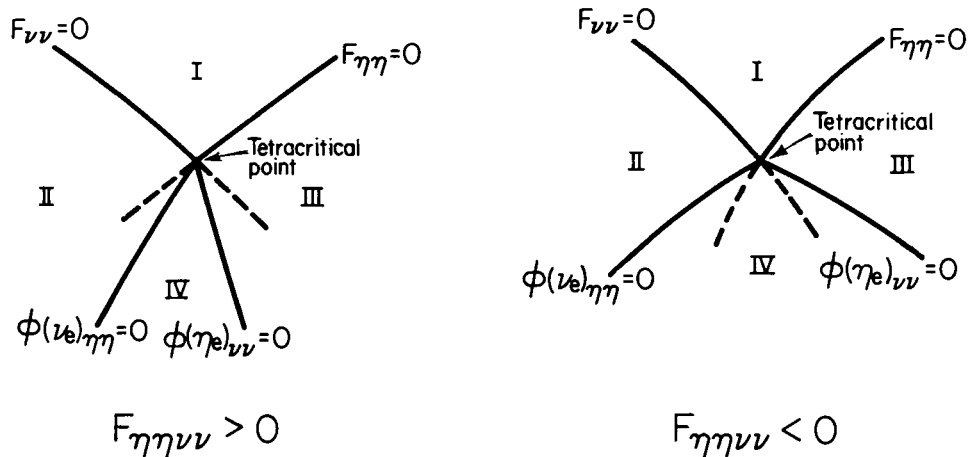
$$\Phi(\eta_e)_{\nu\nu} = F_{\nu\nu} - \frac{3F_{\eta\eta}F_{\eta\eta\nu\nu}}{F_{\eta\eta\eta}} = 0 \quad (\text{Eq 33})$$

we have a phase transition from III to IV. Similarly, the II-IV transition is located along the locus:

$$\Phi(\nu_e)_{\eta\eta} = F_{\eta\eta} - \frac{3F_{\nu\nu}F_{\eta\eta\nu\nu}}{F_{\nu\nu\nu\nu}} = 0 \quad (\text{Eq 34})$$

Note that Eq 33 and 34 differ from the conditions  $F_{\eta\eta} = 0$  and  $F_{\nu\nu} = 0$ , which is where transitions to a singly ordered state occur: i.e., the I-III and I-II transitions, respectively. The loci of the II-IV and III-IV transitions are deflected inward or outward from the I-II and I-III transitions at the intersection point, as illustrated in Fig. 4. The sense of the deflection depends on the sign of  $F_{\eta\eta\nu\nu}$ , as shown by Eq 33 and 34 and depicted in Fig. 4.

Fig. 4 Tetracritical Points



Two versions of tetracritical points can occur, depending on the sign of  $F_{\eta\eta\nu\nu}$ .

Stability of the phases requires that  $\partial^2 F_e / \partial c^2$  be positive. These second derivatives are different in each of the four phases:

$$\begin{aligned}
 F_{cc}^I &= F_{cc}^0 \\
 \Phi_{cc}^{II} &= F_{cc}^0 - 3(F_{\nu\nu c})^2 / F_{\nu\nu\nu\nu} \\
 \Phi_{cc}^{III} &= F_{cc}^0 - 3(F_{\eta\eta c})^2 / F_{\eta\eta\eta\eta} \\
 \Phi_{cc}^{IV} &= F_{cc}^0 - \frac{3[(F_{\eta\eta c})^2 F_{\nu\nu\nu\nu} + (F_{\nu\nu c})^2 F_{\eta\eta\eta\eta} - 6F_{\eta\eta c} F_{\nu\nu c} F_{\eta\eta\nu\nu}]}{F_{\eta\eta\eta\eta} F_{\nu\nu\nu\nu} - 9(F_{\eta\eta\nu\nu})^2}
 \end{aligned}
 \tag{Eq 35}$$

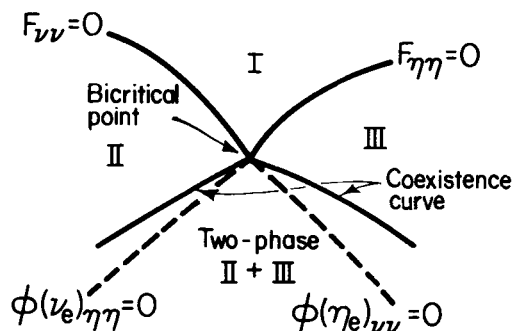
The type of critical point at the crossing of the  $F_{\eta\eta} = 0$  and  $F_{\nu\nu} = 0$  lines can now be discussed. If either  $\Phi_{cc}^{II}$  or  $\Phi_{cc}^{III}$  are negative at the point of intersection, a tricritical point would have occurred elsewhere in the phase diagram. Therefore, the instance where both are positive was examined. If  $\Phi_{cc}^{IV}$  is positive, phase IV is stable with respect to variations in composition, and the point of intersection is a *tetracritical point*, at which the four phases: I, II, III, and IV, become identical. Thus, the solid lines in Fig. 4 give the equilibrium phase diagram in the vicinity of a tetracritical point.

When both  $\Phi_{cc}^{II}$  and  $\Phi_{cc}^{III}$  are positive, but  $\Phi_{cc}^{IV}$  is negative, a miscibility gap originates at the intersection of the lines of critical points, giving rise to a region of two-phase coexistence between phases II and III, as illustrated in Fig. 5. The loci  $\Phi(\nu_e)_{\eta\eta} = 0$  and  $\Phi(\eta_e)_{\nu\nu} = 0$  are limits to metastability with respect to  $\eta$  and  $\nu$  ordering of phases II and III, respectively. In addition they delimit a *conditional spinodal* region in which the doubly ordered state IV is unstable with respect to variations of composition.

### Bragg-Williams Model for CsCl Ordering

The equations for the free energy of a homogeneous phase with the CsCl structure in the Bragg-Williams approximation<sup>18</sup> are reviewed in this section to illustrate for a specific thermodynamic model, the analytic form for  $F$  and the predictions that may be derived from it.

Fig. 5 Bicritical Point



At a bicritical point, a miscibility gap between two ordered phases, II and III, terminates. The two ordering transitions involve different order parameters. I is the disordered phase.

The CsCl structure has two sublattices, denoted by subscripts 1 and 2, with different occupancies by atom species A and B. The order parameter  $\eta$  is defined such that the sublattice concentrations  $c_1$  and  $c_2$  are given by:

$$c_1 = c + \eta$$

and

$$c_2 = c - \eta$$

where  $c$  is the average composition. In the pairwise interaction model, interchange energies per atom for  $i$ 'th neighbor atoms are defined in terms of bond energies,  $E_i^{xy}$ , between a pair of atoms,  $x$  and  $y$ :

$$V_i = \frac{1}{2}(E_i^{AA} + E_i^{BB}) - E_i^{AB}$$

so that  $V_i$  positive favors  $i$ 'th neighbor bonds between unlike atoms. Considering only interactions between atoms

at first and second neighbor distances, the internal energy,  $E$ , and entropy,  $S$ , are expressed by:<sup>19</sup>

$$E = -N\{4[c(1 - c) + \eta^2]V_1 + 3[c(1 - c) - \eta^2]V_2\} \quad (\text{Eq 36})$$

and

$$S = -\frac{1}{2}Nk[(c + \eta) \ln(c + \eta) + (1 - c - \eta) \ln(1 - c - \eta) + (c - \eta) \ln(c - \eta) + (1 - c + \eta) \ln(1 - c + \eta)] \quad (\text{Eq 37})$$

where  $N$  is the number of atoms and  $k$  is Boltzmann's constant. Both  $E$  and  $S$  are even functions of  $\eta$ . Second-order transitions are possible.

All of the derivatives of  $F \equiv E - TS$  with respect to  $c$  and  $\eta$  required for the Landau model are readily obtained and evaluated at  $\eta = 0$  to give:

$$\partial^2 F / \partial c^2 = 2N(4V_1 + 3V_2) + NkT/[c(1 - c)] \quad (\text{Eq 38})$$

$$\partial^2 F / \partial \eta^2 = -2N(4V_1 - 3V_2) + NkT/[c(1 - c)] \quad (\text{Eq 39})$$

$$\partial^3 F / \partial \eta^2 \partial c = -NkT(1 - 2c)/c(1 - c)^2 \quad (\text{Eq 40})$$

$$\partial^4 F / \partial \eta^4 = 2NkT(1 - 3c + 3c^2)/[c(1 - c)]^3 \quad (\text{Eq 41})$$

In the equations that follow, only the circumstances for which  $V_1$  is positive and  $V_2$  is negative are considered. For these interactions, the ground state consists of a pure component plus a stoichiometric CsCl ordered phase.<sup>20</sup>

To locate the locus of order-disorder transitions, Eq 39 is used to solve Eq 28(a) for the curve  $c_\lambda(T)$ :

$$kT = 2(4V_1 - 3V_2)c_\lambda(1 - c_\lambda) \quad (\text{Eq 42})$$

A tricritical point can exist only if there is a point along the locus  $c_\lambda(T)$  where  $\Phi_{cc} = 0$ . Using Eq 27, 38, 40, and 41 to express Eq 28(b) gives the equation for the locus  $c_s(T)$  of the conditional spinodal valid near  $F_{\eta\eta} = 0$ :

$$kT = 4(4V_1 + 3V_2)c_s(1 - c_s) \cdot [1 - 3c_s + 3(c_s)^2]/[1 - 6c_s + 6(c_s)^2] \quad (\text{Eq 43})$$

Combining Eq 42 and 43 gives the expression for the composition  $c_i$  at the intersection of the order-disorder transition with the conditional spinodal:

$$(4V_1 - 3V_2)/(4V_1 + 3V_2) = 2[1 - 3c_i + 3(c_i)^2]/[1 - 6c_i + 6(c_i)^2] \quad (\text{Eq 44})$$

The temperature of the intersection is given by substitution of  $c_i$  for  $c_\lambda$  in Eq 42.

Inspection of Eq 44 shows that the loci  $c_\lambda(T)$  and  $c_s(T)$  intersect only when:

$$V_2/V_1 < -4/9 \quad (\text{Eq 45})$$

By using the Bragg-Williams free energy model to write out Eq 28(c), it can be shown that the composition  $c_i$  in Eq 44 is indeed a tricritical point, and thus that tricritical points result in this model whenever the interaction energies,  $V_1$  and  $V_2$ , obey Eq 45.

The predictions of the Landau model derived above can be compared directly with phase diagrams computed in the Bragg-Williams approximation by Inden.<sup>21</sup> Figures 6(b) to 6(d) of Ref 20 show phase diagrams computed for ratios of

$V_2/V_1$  equal to  $-1$ ,  $-8/3$  and  $-\infty$ , respectively. The values of  $c_i$  computed by Inden are in agreement with those given by Eq 44.

## Coherent Phase Diagrams

Coherent equilibria differ from the ordinary incoherent phase equilibria in an elastic term that is composition, order, and volume fraction dependent. Coherent critical consolute points differ from incoherent ones by tens to hundreds K, consistent with theory. The temperature difference between coherent and incoherent tricritical points has been calculated to have similar magnitudes.<sup>11</sup> Phase diagram calculations<sup>22</sup> for the Fe-Al system show a bicritical point at the intersection of the line of Curie points with an order-disorder transition. This is most likely a multicritical point of the incoherent equilibrium diagram.<sup>23</sup> Coherency strains depress the temperature of coherent phase separation by about 40 K.<sup>10,11,24</sup> Thus, in the coherent diagram, there are two multicritical points: a tetracritical point at the crossing of the lines of order-disorder transitions and Curie points, and a tricritical point at about 40 K lower. In a previous calculation that ignored the magnetic transition and assumed both coherent and incoherent diagrams to have tricritical points, this separation was overestimated at 300 K.<sup>11</sup> The separation due to coherency effects between a bicritical and tricritical point should be much less.

## Discussion

In binary alloys, with pressure fixed, there are not enough degrees of freedom for lines of ordering transitions, each involving one of three different ordering parameters, to intersect at a point. Therefore, the list of critical points given here, which included effects of composition and two order parameters, is all that can be expected according to a Landau theory. All have been seen in alloy systems. The principles in the Landau theory by which the various features arise involve simple calculus. As was demonstrated with an example, the theory is compatible with any model that gives analytic expressions for the free energy.

The Landau theory and most of the theoretical models for alloys give singularities with rational classical exponents. Most of the transitions in solid alloys are expected to give rational exponents. Liquid alloy consolute points and some ordering transitions in solids should have irrational exponents. In such transitions, the second derivative of  $F$  diverges to an integrable infinity instead of having a discontinuity. Phase diagram details that depend on the second derivatives of  $F$  will be different from those derived in the Landau model.

On symmetry arguments, Landau argued that intersections of higher-order transitions must always give rise to a first-order transition and, hence, always to a bicritical point. The Landau expansions, on the other hand, permit tetracritical points. They have been found experimentally and predicted from simple models.

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## Utilization of Phase Diagrams

Phase diagrams are justifiably regarded as an important component of our technological society; the *Bulletin* will publish examples that illustrate their value in the development of new science, trouble shooting, manufacturing control, and the development of new materials. Readers are invited to share their experiences by submitting items to the Editor, in any area of application.

### Historical Note on Use of Phase Diagrams

About one-half century ago, the aluminum industry developed an interest in going into the business of making aluminum screw machine products. None of the aluminum-base alloys then on the market were sufficiently free-machining to be handled by an automatic lathe. However, it was noted that the addition of lead to copper alloys improved their machining characteristics. On this basis,

the phase diagram of the copper-lead system was compared with the phase diagrams of aluminum-base systems. Two were found to be similar to the copper-lead diagram (Fig. 1): namely, aluminum-lead and aluminum-bismuth (Fig. 2). Acting on this knowledge, a series of free-machining aluminum-base alloys was developed using small additions of both lead and bismuth.

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