

Solid solutions under irradiation. I. A model for radiation-induced metastability

R. Cauvin and G. Martin

*Section de Recherches de Metallurgie Physique, Centre d'Etudes Nucleaires de Saclay,
91191 Gif-sur-Yvette Cédex, France*

(Received 5 May 1980)

A simple model for solute concentration fluctuations in solid solutions under irradiation is proposed. The *irreversible* reaction of interstitial-vacancy mutual annihilation at solute clusters is shown to have a destabilizing effect for homogeneous undersaturated solid solutions. Under appropriate irradiation conditions defined by the irradiation flux and temperature, some solute concentration fluctuations become unstable: solute precipitation results. A simple expression for the solvus under irradiation is proposed. Unusual properties of the solute solubility limit under irradiation are predicted. The capability of the model to account for experimental observations is demonstrated in the companion paper.

I. INTRODUCTION

Radiation-induced (as opposed to accelerated) precipitation in *undersaturated* solid solutions is becoming a well-documented phenomenon.¹ Solid solutions which are thermodynamically stable outside irradiation may separate in two distinct phases under appropriate irradiation conditions. The phenomenon was reported in NiSi, NiBe, NiGe, MgCd, AlZn, WRe binary solid solutions and in many industrial alloys. (For industrial alloys, however, the lack of a safe knowledge of the equilibrium phase diagrams makes it difficult to distinguish between radiation-induced and radiation-enhanced precipitation.) Recent reviews are available.^{2,3} Radiation-induced precipitation is one among various radiation-induced phase changes which are expected to occur in appropriate ranges of irradiation flux and temperature.⁴

In many cases, radiation-induced precipitation, which we denote now by RIP, is observed to be heterogeneous: the precipitates form at point defect sinks in NiSi,⁵⁻⁷ in NiBe,⁸ in NiGe.⁹ This type of RIP is successfully interpreted as resulting from the accumulation of solute atoms drifted towards the point defect sinks by the point defect fluxes sustained by irradiation.^{7,10,11}

Recently however, radiation-induced *homogeneous* precipitation was reported, in AlZn,¹² as well as in AISI 316 steels,¹³ or WRe.¹⁴ Moreover, in the AlZn system, RIP may occur in the form of coherent precipitates.¹² Finally, a beautiful small-angle neutron scattering experiment of electron-irradiated NiCu solid solutions has demonstrated the formation, under irradiation, of solute concentration fluctuations with unusual distribution¹⁵: some long-wavelength fluctuations appear after appropriate irradiation.

The above facts call for a general treatment of solute concentration fluctuations in solid solutions

under irradiation. There are three distinct reasons why the distribution of solute concentration fluctuations may be different under irradiation and outside irradiation: First, irradiation induces disorder by replacement collisions in the crystal. Up to now, this effect has been thought to be at the origin of second-phase resolution. Second, irradiation sustains in the solid solution a high point-defect concentration: a binary solid solution under irradiation is therefore rather a quaternary system (solvent-solute-vacancy interstitials). Several attempts for a strictly thermodynamical description of solid solution destabilization under irradiation have been published.¹⁶⁻²⁰ To our knowledge, none of these could account for the observed results: the disagreement is at least quantitative^{17-19,21} and sometimes qualitative, in the sense that some condition, which is found to be necessary for a model binary solid solution to be destabilized by a small point-defect addition, is not fulfilled by those systems where RIP is observed.²⁰ Finally, since point defects are nonconservative species, (even in the absence of point-defect sinks, they eliminate by mutual recombination), a solid solution under irradiation may be viewed as an open reactive-diffusive system which reaches a *steady state* rather than an equilibrium state. With this idea in mind, there is no *a priori* reason why the solute concentration fluctuations under irradiation should behave as in a closed system.²²

Indeed we have demonstrated elsewhere²³ that the *instability* limit for a solid solution (the "chemical spinodal") may be shifted towards lower solute concentrations due to the vacancy-interstitial mutual annihilation reaction. In other words, for a *given point-defect concentration*, a solid solution may be (linearly) stable from a strictly thermodynamical viewpoint and (linearly) unstable if the vacancy-interstitial recombination reaction is taken into account. We have given

elsewhere¹² one possible atomic mechanism for the amplification of solute concentration fluctuations by vacancy-interstitial mutual annihilation.

In practice, however, it is still a matter of discussion to decide whether the instability limit of a solid solution can be observed experimentally, or is it simply a heuristic theoretical concept (for recent discussion, cf. Ref. 24). In any case, the experimentally observed solvus corresponds to a stability limit, beyond which the solid solution is first *metastable* due to the existence of a nucleation barrier. It is therefore important to study radiation induced *metastability* as a complement to our previous work, which concerned *instability*.²³

The purpose of this article is to propose a model of solute concentration fluctuations in a solid solution under irradiation and to elucidate what the conditions are for an irradiation to destabilize a solid solution.

This problem may be addressed by two different techniques. The first one rests on a continuum description of the solid solution: the state of the solid solution is described by the concentration profiles of the elements throughout the system. This type of description is most efficient for the treatment of solid solution *instability*,²⁵⁻²⁸ and was adopted in our previous work.²³ In principle at least, a concentration profile description of the state of a solid solution can be used to study solid solution *metastability* as well.^{26,29-31} Such a description however is mathematically very involved since full account must be taken of nonlinearity in order to describe the large "hetero-phase fluctuations" which destabilize the solid solution. On the other hand a cluster description of solute concentration fluctuations is well suited for describing solid solution *metastability*, at least as long as the solid solution is sufficiently dilute to avoid the percolation problem (for a recent review cf. Ref. 32). With this type of description, the state of the solid solution is specified by the size distribution of the solute clusters it contains. When the solid solution is in a metastable state, the cluster-size distribution separates into two parts: small clusters with an approximately steady distribution and larger ones which grow as time passes: the small clusters represent the concentration fluctuations in the solid solution, while the larger ones represent the growing precipitates.³³

In this work we chose a cluster description of the state of the solid solution and show how the irreversible vacancy-interstitial mutual annihilation reaction affects the solute cluster distribution. An attempt in the same direction has already been published³⁴: the model, however, predicts RIP for *incoherent* precipitates only, and large decrease of the solubility limit are expected for those systems only where the precipitate atomic volume is *larger* than that of the solvent matrix. The above two limitations are violated by the AlZn system which exhibits undersized coherent precipitates formation^{1,12} and are not required for the

present model.

In the next section we present the solid solution model and the simplifying assumptions which we use. A qualitative explanation of the driving force for RIP will then emerge. The third section, deals with the mathematical treatment of the model; the condition for radiation-induced metastability is obtained, as well as a simplified equation for the solvus under irradiation. In the fourth section we discuss in a semiquantitative way the shape of the solvus under irradiation, and the behavior of the solid solution in the radiation induced metastability regime. In particular, we demonstrate that the lever rule for the amount of precipitation need not be obeyed, according to this model. In the last section we discuss the limitations of the present model. The detailed comparison of the model to experimental results is dealt with in a companion paper.¹

II. MODEL FOR SOLUTE CONCENTRATION FLUCTUATIONS UNDER IRRADIATION

A. Solid solution model

We describe the state of the solid solution under irradiation by a distribution of clusters embedded in the solvent. A large set of parameters is necessary to give a detailed description of the clusters: number of solute atoms, number of vacancies, number of interstitials, shape, relative location of the species inside the cluster, etc. If our aim were to predict the evolution of the overall microstructure of the solid solution during irradiation, all the above parameters should be retained: indeed depending on the shape of a cluster quite different microstructural evolutions might result (e.g., void instead of vacancy loops, etc.). Such a description is beyond the goal of the present work. The model we present is simply aimed at elucidating the mechanism and conditions for RIP. We therefore assume that no defect clustering occurs, or at least that defect clustering, if any, does not interfere with solute clustering.

More precisely we view the clusters as *solute aggregates embedded in a gas of point defects*, some of which may get trapped at the periphery of the aggregate. We further simplify the model by assuming that vacancies and interstitials cannot coexist on a given cluster. A cluster is therefore specified by the number s of solute atoms it contains and a number of trapped defects d . We represent a cluster in a solute defect diagram (Fig. 1): by convention we locate the clusters with d trapped interstitials on the positive side of the defect axis, and vice versa for vacancy type clusters. We call $\rho(+d,s)$ [respectively, $\rho(-d,s)$] the densities of clusters which contain s solute atoms and which have trapped d interstitials (respectively, d vacancies).

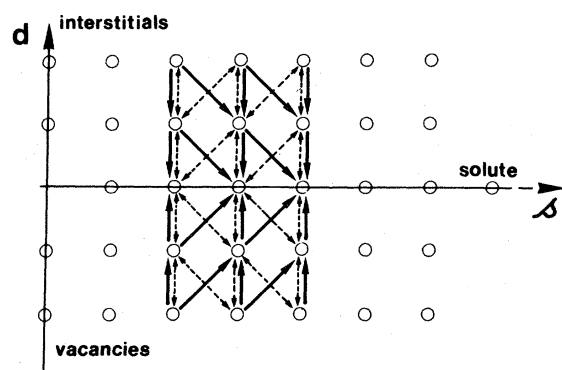


FIG. 1. Cluster space: <----> reversible reactions, — irreversible reactions.

The history of a cluster can therefore be represented by a trajectory in the d,s plane (Fig. 1). The clusters propagate in this plane by impinging and emitting point defects and solute atoms. For the sake of simplicity we assume that only eight elementary reactions contribute to the cluster propagation: (a) single vacancy adsorption or emission, (b) solute adsorption or emission by vacancy diffusion mechanism (i.e., absorption or emission of a vacancy-solute pair), (c) simple interstitial adsorption or emission, (d) solute adsorption or emission by interstitial diffusion mechanism (i.e., absorption or emission of a mixed dumbbell). Before going into more details, simple inspection of Fig. 1 allows for a qualitative understanding of the mechanism of the destabilization of solid solution by the irreversible vacancy-interstitial annihilation reaction. Indeed for given vacancy and interstitial concentrations, let us compare two different regimes for the solid solution: in the first regime, no vacancy-interstitial annihilation is allowed. The possible "jumps" of the clusters among the lattice points of the (d,s) plane are reversible as shown by the dotted arrows on Fig. 1. The system will reach some equilibrium configuration which we assume to be that of a uniform solid solution: in other words, the concentration of clusters decreases as their solute content increases. In the second regime, irreversible vacancy-interstitial mutual annihilation is allowed (and must be compensated by a steady point defect production by irradiation). Irreversible "jumps" result for the cluster (solid arrows Fig. 1) such as (i) the loss of one vacancy (respectively, interstitial) by the capture of one interstitial (respectively, vacancy) at a vacancy (respectively, interstitial) type cluster; (ii) the addition of one solute together with the destruction of one trapped defect by the arrival of a solute by vacancy (respectively, interstitial) diffusion mechanism at an interstitial (respectively, vacancy) type cluster. The result of the irreversible jumps is twofold: they drive the clusters

towards the solute axis, and along this axis towards larger solute content. Is this latter driving force sufficient to induce metastability for a thermodynamically stable solid solution? The answer is yes, as will be shown in the next section, by a detailed evaluation of the cluster flux in the d,s plane.

We are faced with a problem of multiframe nucleation³⁵ as is usually the case for the description of various clustering events under irradiation.^{34, 36, 37} The crucial point in such models is the choice of the expression for the free energy change on forming a cluster (d,s) which yields the equilibrium distribution of clusters. A general description of this distribution is beyond the goal of this paper. We rather make some more simplifying assumptions which render the model easily tractable analytically.

B. Simplifying assumptions

We further simplify the description by assuming that the solute-defect interaction is sufficiently weak compared to solute-solute interactions, for the equilibrium distribution of the solute cluster sizes to be unaffected by the defect population. Therefore, at equilibrium (where the ρ take the values $\bar{\rho}$), the overall density of clusters with s solute atoms

$$\bar{\rho}_i(s) = \sum_{d=1}^{Z(s)} [\rho(+d,s) + \rho(-d,s)] + \rho(0,s) \quad (1)$$

is independent of the free defect concentrations $\rho(\pm 1, 0)$. In other words

$$\bar{\rho}_i(s) = N \exp[-\Delta G(s)/kT] \quad (2)$$

with $\Delta G(s)$ the free-energy change on forming a solute aggregate of s solute atoms in the absence of point defects, and N the number of lattice sites per unit volume.

In the presence of point defects, but with no vacancy-interstitial recombination allowed, and no vacancy and interstitial cohabitation on a single cluster permitted, the equilibrium cluster concentration is [cf. Appendix A, Eq. (A14)]

$$\bar{\rho}(\pm d,s) = \bar{\rho}_i(s) \frac{Z(s)!}{d! [Z(s) - d]!} \left(\frac{p_{\pm}}{1 - p_{\pm}} \right)^d \frac{1}{N(s)} \quad (3)$$

$Z(s)$ is the number of trapping centers for defects at a solute aggregate with s atoms; p_{\pm} is the occupation probability of a trapping center by an interstitial (p_+) or a vacancy (p_-)

$$p_{\pm} = \Omega \rho(\pm 1, 0) \exp(-g_{\pm}^B/kT) \quad (4)$$

where Ω is the atomic volume, g_{\pm}^B is the binding free energy for an interstitial (+) or a vacancy (-) at a trapping center, and $N(s)$ is a normalization factor,

which ensures that $\bar{\rho}_r(s)$ is unaffected by defect trapping at the clusters. The expression of $N(s)$ is given by Appendix A [Eq. (A13)], Eq. (3) is valid in the limit of small p_{\pm} and of vanishing defect-defect interaction energy.

When vacancy-interstitial recombination is allowed for, we further assume that the solute clusters are still in equilibrium with the point-defect population: i.e., we assume that the arrival and departure of free defects at the clusters are much more frequent than those of solute atoms. Therefore

$$\rho(\pm d, s) = \rho_r(s) \frac{Z(s)!}{d! [Z(s) - d]!} \left(\frac{p_{\pm}}{1 - p_{\pm}} \right)^d \frac{1}{N(s)} \quad (5)$$

The above hypothesis might be relaxed in a numerical computation. Work is in progress now. But the basic understanding and right order of magnitude can be reached with this simple model as will be seen in the companion paper.¹

With the above hypotheses we may turn to a simple discussion of radiation induced metastability.

III. CONDITION FOR RADIATION-INDUCED METASTABILITY

Since we are interested in solute precipitation, we focus attention on the cluster flux *along the solute axis* (Fig. 1). The expression for this latter flux is established in Sec. III A and yields the condition for metastability as shown in Sec. III B.

A. Cluster flux along the solute axis

The cluster flux along the s axis, $J(s \rightarrow s+1)$ is the balance between the total density of clusters with

$$J(s \rightarrow s+1) = \rho_r(s) [\beta_+(s) + \beta_-(s)] - \{ \alpha_+(s+1) \rho_r(s+1) [(1-p_+)^{-Z(s+1)} - 1] + \alpha_-(s+1) \rho_r(s+1) [(1-p_-)^{-Z(s+1)} - 1] \} N(s+1)^{-1} \quad (7)$$

As usual, we lack an *ab initio* expression for the emission coefficients $\alpha_+(s)$, $\alpha_-(s)$. But we can reasonably assume that they are typical of the cluster itself, so that they may be calculated from the condition of detailed balance at equilibrium, in the absence of vacancy-interstitial recombination: under such conditions the cluster flux along the s axis must be zero for each diffusion mechanism taken individually. For interstitial (+) as well as vacancy mechanism (-) the cluster flux writes:

$$J_{\pm}(s \rightarrow s+1) = \beta_{\pm}(s) \rho_r(s) (1 - p_{\pm})^{-Z(s)} N(s)^{-1} - \alpha_{\pm}(s+1) \rho_r(s+1) \times [(1 - p_{\pm})^{-Z(s+1)} - 1] N(s+1)^{-1} \quad (8)$$

s solute atoms which impinge one solute atom per unit time and the corresponding number of clusters with $(s+1)$ solute atoms which lose one solute atom, whatever the number of point defects which are trapped at the solute clusters.

$$J(s \rightarrow s+1) = [\beta_+(s) + \beta_-(s)] \rho_r(s) - \sum_{d=1}^{Z(s+1)} [\rho(+d, s+1) \alpha_+(s+1) + \rho(-d, s+1) \alpha_-(s+1)] \quad (6)$$

In this equation, $\beta_+(s)$ and $\beta_-(s)$ are, respectively, the arrival rates of solute by interstitial or vacancy diffusion on a cluster which contains s solute atoms, $\alpha_+(s)$ and $\alpha_-(s)$ are, respectively, the rate of solute emission by interstitial or vacancy mechanism from a cluster with s solute atoms. [A term $-\beta_+(s) \rho(Z, s) - \beta_-(s) \rho(-Z, s)$ should be added if $Z(s+1) < Z(s) + 1$. It has been omitted in the right-hand side of Eq. (6) and it is negligible for $p_{\pm} \leq 0.5$ and $Z \geq 5$, as is obvious from Eq. (5).] When establishing Eq. (6), we have assumed that neither the impingement rates β nor the emission rates α depend on the defect content of the cluster. Notice that the summation starts from $d=1$ since no solute atom can be emitted from a defect-free cluster. We may as well choose α_{\pm} to be proportional to the defect content of the cluster [$\alpha(\pm d, s) = d \alpha_{\pm}(s)$]. The final form of the cluster flux [Eqs. (10), (11a), (11b)] is unaffected. Indeed, the detailed form of α will be eliminated owing to the detailed balance argument [cf. Eq. (9) below].

According to the expression of $\rho(d, s)$, p_{\pm} , and the definition of $\bar{\rho}_r(s)$ [Eqs. (1)–(4)], Eq. (6) may be rewritten as

since $\rho_r(s) (1 - p_{\pm})^{-Z} N(s)^{-1}$ is the total number of clusters of interstitial (+) or vacancy (-) type with s solutes when vacancy-interstitial cohabitation at a cluster is forbidden [Appendix A Eq. (A15)]. At equilibrium, $J_{\pm} = 0$ and

$$\alpha_{\pm}(s+1) = \beta_{\pm}(s) \frac{\bar{\rho}_r(s)}{\bar{\rho}_r(s+1)} \times \frac{(1 - p_{\pm})^{-Z(s)}}{[(1 - p_{\pm})^{-Z(s+1)} - 1]} \frac{N(s+1)}{N(s)} \quad (9)$$

where $\bar{\rho}_r(s)$ is the equilibrium concentration defined by Eq. (2). Introducing Eq. (9) into Eq. (6) yields

$$J(s \rightarrow s+1) = \rho_r(s) A(s) \left[1 - \frac{\rho_r(s+1)}{\rho_r(s)} \frac{\bar{\rho}_r(s)}{\bar{\rho}_r(s+1)} B(s) \right], \quad (10)$$

with

$$A(s) = \beta_+(s) + \beta_-(s), \quad (11a)$$

$$B(s) \left[\frac{\beta_+(s)}{\beta_-(s)} \left(\frac{1-p_-}{1-p_+} \right)^{z(s)} + 1 \right] / \left[1 + \frac{\beta_+}{\beta_-} \right] \left[1 + \left(\frac{1-p_-}{1-p_+} \right)^{z(s)} - (1-p_-)^{z(s)} \right]. \quad (11b)$$

Equation (10) together with the definitions (11) is the basic equation of the problem. As is usual in the classical nucleation theory, Eq. (10) may be interpreted as describing a diffusion and convection flux of particles along the s axis, with a position dependent diffusion coefficient $A(s)$, and a force field which derives from the effective potential:

$$\tilde{G}(s) = -kT \ln \bar{\rho}_r(s) \quad (12)$$

with $\bar{\rho}_r(s)$ solution of the equation

$$\frac{\bar{\rho}_r(s)}{\bar{\rho}_r(s+1)} = \frac{\bar{\rho}_r(s)}{\bar{\rho}_r(s+1)} B(s). \quad (13)$$

[As can be seen in Eq. (11), $B(s)$ involves equilibrium (p_+, p_-) as well as kinetic parameters (β_+ and β_-). $\tilde{G}(s)$ is therefore not a thermodynamical potential. It is simply a useful intermediate variable in the computation.] According to the assumptions of Sec. II B [Eq. (2)], Eq. (13) may be written

$$\frac{\bar{\rho}_r(s)}{\bar{\rho}_r(s+1)} = B(s) \exp \frac{\partial \tilde{G}(s)}{kT \partial s}, \quad (14)$$

where $G(s)$ stands for $\Delta G(s)$ in Eq. (2) in order to simplify the writing. The condition for radiation-induced metastability can be deduced in a straightforward manner from the above interpretation of the cluster flux. The technique is very similar to that used by Russell for the theory of void nucleation under irradiation.³⁸

B. Condition for solid solution metastability

According to the above discussion, the solid solution is in a metastable state whenever the effective potential $\tilde{G}(s)$ exhibits a maximum for some critical solute cluster size s^* . As shown by Eqs. (12) and (13), s^* is such that

$$\frac{\partial \tilde{G}}{\partial s} \Big|_{s^*} = \frac{\partial G}{\partial s} \Big|_{s^*} + kT \ln B(s^*) = 0. \quad (15)$$

In order to elucidate the nature of the critical point s^* defined by Eq. (15), the behavior of $\partial \tilde{G} / \partial s$ in the vicinity of s^* must be studied. As shown in the Appendix B, $B(s)$ may exhibit two different behaviors,

according to the sign of

$$\mathfrak{S} = (1 - p_+/p_-)(1 - \beta_+/\beta_-). \quad (16)$$

When $\mathfrak{S} < 0$, $B(s)$ is a decreasing function of s (Fig. 2). $B(s)$ decays from 1 to B_∞ as s increases from zero to infinity. When $\mathfrak{S} > 0$, $B(s)$ first decreases from 1 to B_{\min} , which is always larger than $\frac{1}{2}$, and then increases to B_∞ , which is always smaller than 1 (Fig. 2).

B_∞ has the following expressions:

$$B_\infty = \begin{cases} (1 + \beta_-/\beta_+)^{-1} & \text{for } p_+ > p_- \quad (17a) \\ (1 + \beta_+/\beta_-)^{-1} & \text{for } p_- > p_+ \quad (17b) \\ \frac{1}{2} & \text{for } p_- = p_+ \quad (17c) \end{cases}$$

Equation (15) has a simple graphical interpretation depicted in Fig. 3. Assuming $G(s)$ has the classical form:

$$G(s) = s \Delta \mu(C) + s^{2/3} \sigma \gamma, \quad (18)$$

where $\Delta \mu(C)$ is the difference of the solute chemical potential between the solid solution with a solute concentration C and the precipitate, σ the precipitate-matrix interface energy and γ a geometrical factor, we find:

$$\frac{\partial G(s)}{\partial s} = \Delta \mu(C) + \frac{2}{3} s^{-1/3} \sigma \gamma. \quad (19)$$

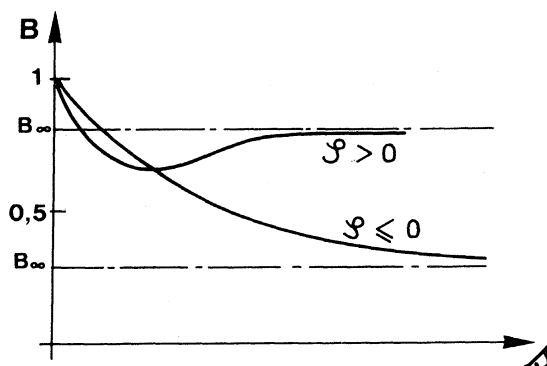


FIG. 2. Shape of $B(s)$, when $\mathfrak{S} < 0$ (a) or when $\mathfrak{S} > 0$ (b).

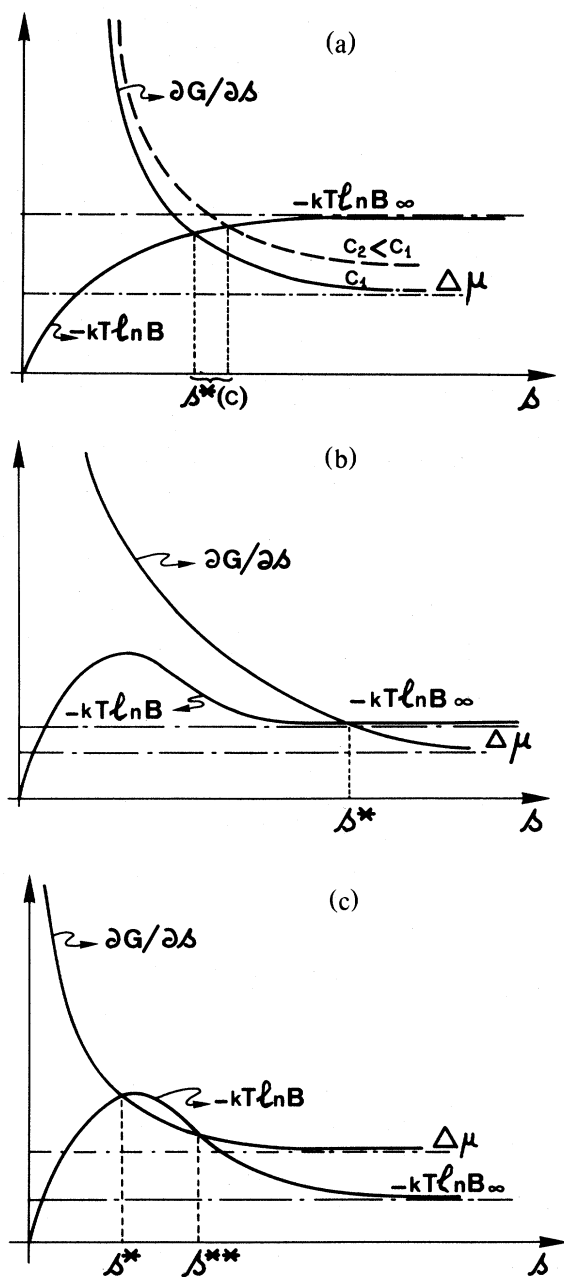


FIG. 3. Graphical construction of the critical cluster size, when $S < 0$ (a), or when $S > 0$ (b) and (c). In (a), B is assumed to be independent of the solute concentration C in the matrix.

In an undersaturated solid solution $\Delta\mu > 0$, so that $\partial G/\partial s$ in the right-hand side (RHS) of Eq. (19) decreases from infinity towards a constant positive value, $\Delta\mu$, as s increases. Moreover, the more dilute the solid solution, the higher $\Delta\mu$. As shown by Fig. 3, a sufficient condition for Eq. (15) to have a posi-

tive solution is that $C > \bar{C}$ where \bar{C} is defined by

$$-kT \ln B_\infty = \Delta\mu(\bar{C}) \quad (20)$$

When \bar{C} exists, s^* as defined by Eq. (15) is a saddle point. Indeed as can be seen in Fig. 3, $\partial\bar{G}/\partial s$ is first positive and then negative as s increases. The critical fluctuation is in unstable equilibrium ($\partial^2\bar{G}/\partial s^2|_{s^*} < 0$). Sufficient condition for solid solution metastability are therefore (i) that Eq. (20) has a solution, and (ii) that the solute content is larger than \bar{C} . Equation (20) therefore defines the solute solubility limit under irradiation. Equation (20) is an implicit equation for \bar{C} . Indeed, for given irradiation flux and temperature, the point-defect concentrations reach a steady-state value $\rho(1,0)$ and $\rho(-1,0)$ which depend on solute concentration since the defect mobilities and therefore the defect recombination rates are affected by trapping at the solute atoms. The steady-state value of the defect concentrations, together with the temperature determine the values of p_\pm and β_\pm and therefore of B_∞ .

Before closing this section, it is worth noticing that Fig. 3 suggests the possibility for an unusual behavior of solid solutions under irradiation. As shown in Fig. 3(c), in some rare cases, it is possible that two critical sizes s^* and s^{**} occur. For $s = s^*$ [Fig. 3(c)] the cluster is unstable and either dissolves or grows up to the size s^{**} which is a stable size: indeed at s^{**} , $\partial\bar{G}/\partial s$ is negative for subcritical and positive for supercritical clusters. A necessary condition for this to occur is that $S < 0$.

In the next section, we give a simplified form of Eq. (20) and discuss qualitative features of the solubility limit under irradiation, which result.

IV. SOLUBILITY LIMIT UNDER IRRADIATION

In this section, we give a crude approximation for the equation of the solvus under irradiation, which allows for a qualitative prediction of the shape of this solvus together with the important prediction that the lever rule for the amount of precipitation need not be obeyed under irradiation.

A. Shape of the solvus under irradiation

Assuming an ideal behavior of the solid solution below the solubility limit, $\Delta\mu$ in Eq. (18) can be approximated by

$$\Delta\mu = -kT \ln C/\bar{C} \quad (21)$$

where \bar{C} is the solubility limit in the absence of vacancy-interstitial recombination. Therefore the solvus equation under irradiation is simply

$$\bar{C} = \bar{C}B_\infty \quad (22)$$

Moreover, B_∞ can be given a more suggestive form than in Eq. (17). Indeed, the solute impingement rates β_+ and β_- are proportional to the solute diffusion coefficients by, respectively, interstitial—(D_s^i) and vacancy—(D_s^v) mechanism. The latter coefficients can be written, in the limit of weak solute-defect binding, as

$$D_s^i = a_i D_i C_i, \quad D_s^v = a_v D_v C_v, \quad (23)$$

where C_α and D_α , ($\alpha = i$ or v) are, respectively, the concentration and diffusion coefficient of untrapped defect of type α ; a_α is a correction factor which accounts for the solute-defect binding and for the correlation between successive solute jumps. The coefficients a_α have been evaluated for the vacancy diffusion mechanism³⁹ and for the interstitial diffusion mechanism where the interstitial has a $\langle 100 \rangle$ dumbbell configuration.⁴⁰ a_i and a_v are functions of the point-defect jump frequencies only. They do not vary with the point-defect concentrations.

$D_i C_i$ and $D_v C_v$ can be evaluated from the balance equations for point defects in the solid solution under irradiation (cf. Appendix C). Under steady-state conditions, for unbiased point defect sinks and in the limit of weak point-defect trapping, the following relation holds:

$$D_i C_i \approx D_v (C_v - C_v^0), \quad (24)$$

where C_v^0 is the thermal equilibrium vacancy concentration. Equation (23) together with Eqs. (24) and (17) give:

$$B_\infty \approx \left\{ 1 + \left[\frac{a_i}{a_v} \left(1 - \frac{1}{S_v} \right) \right]^x \right\}^{-1}, \quad (25a)$$

where the value of x is one with the sign of ($p_- - p_+$)

$$x = 1 \operatorname{sgn}(p_- - p_+) \quad (25b)$$

and S_v is the vacancy supersaturation

$$S_v = C_v / C_v^0. \quad (25c)$$

From Eq. (25), we can anticipate the following behavior for the solvus under irradiation:

At "high temperature," the radiation produced point defects eliminate very rapidly, $C_v \rightarrow C_v^0$ and $C_i \rightarrow 0$ according to Eq. (24). As a consequence, $p_+ \rightarrow 0$ while p_- remains finite [$p_- \rightarrow C_v^0 \exp(-g_-/kT)$] so that $x = +1$ [Eq. (25b)]. Therefore $B_\infty \rightarrow 1$ [Eq. (25a)], and the solubility limit is unaffected by irradiation. The high-temperature threshold for radiation-induced precipitation is of course *flux dependent*. The higher the irradiation flux, the higher the temperature limit for which $\bar{C} \rightarrow \bar{C}$ since a higher defect elimination rate is necessary to compensate the higher defect production rate.

TABLE I. Shift of solute solubility limit (\bar{C}/\bar{C}) at low temperature, for limiting values of a_0/a_v .

x	a_i/a_v	
	0	∞
+	1	0
-	0	1

At "low temperature," the vacancy supersaturation S_v becomes very large and B_∞ becomes a *function of temperature only*

$$B_\infty \rightarrow \left[1 + \left(\frac{a_i}{a_v} \right)^x \right]^{-1}. \quad (26)$$

Table I summarizes typical behaviors which may be predicted in the case where a_i or a_v becomes small at low temperature (e.g., due to "caging" for interstitial diffusion by a mixed dumbbell mechanism.⁴⁰) In particular, the solute solubility goes to zero when the defect giving the lower-trapping probability [p_\pm Eq. (4)] causes the higher solute diffusivity, in agreement with the qualitative discussion of Sec. II A. Inversely, the solute solubility is unaffected when the defect with the highest trapping probability causes the highest solute diffusivity.

Some of the above qualitative features are indeed exhibited by the solvus of Zn in Al under electron irradiation as will be shown in the companion paper.¹

B. Steady-state precipitate volume fraction

As shown by Eqs. (22) and (25), for a given temperature, the higher the vacancy supersaturation, the lower the solubility limit. The vacancy supersaturation itself is determined by the irradiation flux, but also by the density of sinks and *immobile trapping centers* for point defects (for a review, see Ref. 41). The more numerous the sinks or traps, the smaller the free vacancy supersaturation. Nevertheless the control parameters for the system are the irradiation flux and temperature but not the sink and trap density since the latter usually evolves during irradiation. Therefore under fixed irradiation conditions, if the solubility limit in the system is exceeded, precipitates will form, at the expense of isolated solute atoms. According to the model, the surface sites of the precipitate are immobile trapping centers for the point defects. Therefore the occurrence of precipitation diminishes the free vacancy supersaturation: as a consequence, the solubility limit in the solid solution containing precipitates may be higher than without precipitates. Radiation-induced precipitation may

thus saturate before the solute content of the solid solution between the precipitates has reached the solubility limit in the absence of precipitates: the latter quantity is the threshold solute content above which a homogeneous solid solution separates into two phases.

As a result of the above discussion, the lever rule for determining the precipitate volume fraction need not be obeyed under irradiation. Such a behavior is observed in the AlZn system,¹ and was already anticipated for radiation-induced segregation at point-defect sinks.⁴²

C. Solute distribution in undersaturated solid solutions under irradiation

In those solid solutions which remain single phase under irradiation ($C < \bar{C}$), the solute cluster distribution differs from that predicted at thermodynamical equilibrium [Eq. (2)]. Indeed at equilibrium under irradiation, the cluster flux in the s direction is zero or according to Eq. (10)

$$\frac{\rho_i(s+1)}{\rho_i(s)} = \frac{\bar{\rho}(s+1)}{\bar{\rho}(s)}, \quad (27)$$

where $\bar{\rho}$ is defined by Eq. (13). Notice that $\bar{\rho}(s)$ is defined by a first-order differential equation. The integration constant is provided by the conservation of solute.

As shown by Eq. (27), the solute distribution at steady state under irradiation is different from that at thermal equilibrium. This should be revealed by experimental studies of local order [x-ray or neutron scattering, extended x-ray absorption fine structure, (EXAFS), etc.]. As a general trend, one expects more larger clusters than at thermal equilibrium. In practice, however, replacement collision sequences under irradiation will destroy short-range correlation between the components and a more detailed study is necessary in order to predict the steady-state degree of short-range order in a single-phase solid solution under irradiation.

V. SUMMARY AND DISCUSSION

We have proposed a simple model for solute concentration fluctuations in a solid solution under irradiation. The fluctuations are represented by solute aggregates which offer trapping centers for the point defects. It is assumed that the solute-solute and cluster-defect binding energies are such that the equilibrium cluster size distribution is independent of the point-defect concentration, when the point defects are treated as conservative species.

When vacancy-interstitial mutual recombination occurs, an extra driving force for solute cluster growth

appears: indeed, every time a solute cluster with an interstitial (respectively, vacancy) trapped receives a solute atom via vacancy (respectively, interstitial) diffusion, a solute atom is added to the cluster and the defect which might allow solute migration away from the cluster is destroyed due to the vacancy-interstitial irreversible mutual annihilation. In an undersaturated solid solution, this driving force for cluster growth opposes the thermodynamical force for the dissolution of large clusters.

Under appropriate conditions [Eq. (20)], i.e., when such events are frequent enough, the new driving force overcomes the thermodynamical force: this, however, is the case for those solute clusters only, the size of which is larger than a critical size [Eq. (15)]. The solid solution then becomes *metastable* with respect to solute concentration fluctuations.

The solute solubility limit is therefore a function of the temperature and of the point-defect supersaturation in the system [Eq. (20)] or more simply [Eqs. (22) and (25)]. The latter quantity is, however, not controlled directly: it is a function of the irradiation flux and of the point-defect sink and trap density. The latter parameter changes as precipitation proceeds. Several important features result (Sec. IV): (i) At high temperature the solubility limit decreases when increasing the irradiation flux. (ii) At low temperature the solubility limit is a function of temperature only. (iii) The precipitation may saturate before the solute content in the matrix between the precipitates has reached the solubility limit. This unexpected behavior might suggest that the stable state of a solid solution under irradiation does not correspond to an extremum of some function of the control parameters of the system (composition, irradiation flux, and temperature).

The above model is very crude in many respects: (i) The equilibrium distribution of clusters of various composition is given a very simple form in the absence of vacancy-interstitial recombination [Eqs. (2) and (3)]. (ii) In the presence of vacancy-interstitial recombination, we assume that the solute clusters remain in equilibrium with the surrounding free-defect gas. (iii) We have neglected the defect-defect binding in favor of solute-defect and solute-solute binding. (iv) We have ignored the details of the trajectories of the clusters in the solute defect phase space.

Therefore the model does not give information on the nucleation rate, nor on the role of solute atoms in catalyzing defect clustering. Similarly, the model does not predict radiation-induced precipitate resolution. Apart from sputtering effects^{43,44} which might be included in a straightforward manner in Eq. (6), we had predicted a new mechanism for the damping of solute concentration fluctuations under irradiation¹²: damping should be possible when the solute clusters attract the point defects and the solute and

defect fluxes are coupled negatively. In the present model the coupling between solute and defect fluxes is described in a crude way to account for the former effect. Work is in progress to overcome the above weaknesses.

The model is, however, detailed enough to demonstrate that the irreversibility of the vacancy-interstitial mutual annihilation reaction may bring a thermodynamically stable solid solution into a metastable state.

In a previous work,²³ we had demonstrated that, for the same reasons, a (linearly) unstable state could be reached beyond some critical irradiation conditions (flux and temperature). The present work points to the existence of metastable states which in principle at least, might have been discovered by a bifurcation analysis of the solution of the balance equations of the previous work. The cluster description which we have used is far more tractable than such a bifurcation analysis and might be of interest in other problems of the field of nonequilibrium phase transitions.

Finally, despite the crude approximations just mentioned, the model accounts qualitatively and with the right order of magnitude for the radiation-induced modification of the Zn solubility in AlZn alloys, as shown in the next paper.¹

ACKNOWLEDGMENTS

The authors gratefully acknowledge the stimulating interest of Dr. Y. Adda in this problem, and several enlightening discussions at various stages of this work, with Professor D. de Fontaine, Professor K. C. Russell and Dr. M. Baron, Dr. A. Barbu, and Dr. J. L. Bocquet.

APPENDIX A: CLUSTERS STATISTICS

Let $\rho_i(s)$ be the density of solute aggregates containing s solute atoms. Each of this aggregates offers $Z(s)$ trapping centers for point defects. In the absence of defect-defect interaction, all trapping centers can be considered as independent traps. The probability that one trap is occupied by one point defect is

$$p = \frac{c \exp(-g/kT)}{1 - c + c \exp(-g/kT)} \quad (\text{A1})$$

where c is the free defect concentration and g the free energy of binding of the defect at the trap ($g < 0$ for an attraction). In the limit of small free defect concentration ($c \ll 1$) and weak binding ($-g/kT \ll 1$) Eq. (A1) reduces to

$$p \approx c \exp(-g/kT) \quad (\text{A2})$$

The trapping centers are grouped into subsets of

$Z(s)$ centers: the peripheral sites of a cluster of s solute atoms. The probability that one of this subset contains d defects is given by a binomial function P of parameters $Z(s)$ and p :

$$P(d, Z, p) = \frac{Z(s)!}{d! [Z(s) - d]!} p^d (1-p)^{Z-d} \quad (\text{A3})$$

Therefore the density of clusters with d defects and s solute atoms is

$$\rho(d, s) = P(d, Z, p) \rho_i(s) \quad (\text{A4})$$

or

$$\rho(d, s) = \rho_i(s) \frac{Z(s)!}{d! [Z(s) - d]!} \left(\frac{p}{1-p} \right)^d (1-p)^{Z(s)} \quad (\text{A5})$$

In particular

$$\rho(0, s) = \rho_i(s) (1-p)^{Z(s)} \quad (\text{A6})$$

so that $\rho(d, s)$ may be rewritten

$$\rho(d, s) = \rho(0, s) \frac{Z(s)!}{d! [Z(s) - d]!} \left(\frac{p}{1-p} \right)^d \quad (\text{A7})$$

When two types of defects are present, with binding energies and trapping probabilities, respectively, labeled by g_{\pm} , p_{\pm} and if we impose that defects of opposite sign cannot cohabit on a single cluster, the density of clusters with d defects and s solute atoms can be written by analogy with Eq. (A4) as

$$\rho(+d, s) = \rho_+(s) P(d, Z(s), p_+) \quad (\text{A8a})$$

$$\rho(-d, s) = \rho_-(s) P(d, Z(s), p_-) \quad (\text{A8b})$$

where $\rho_+(s)$ and $\rho_-(s)$ are normalization factors with the following properties

$$\rho(+0, s) = \rho(-0, s) = \rho(0, s) \quad (\text{A9})$$

that is, according to Eq. (A3)

$$\rho_+(s) (1-p_+)^Z = \rho_-(s) (1-p_-)^Z = \rho(0, s) \quad (\text{A10})$$

and

$$\sum_{n=-Z(s)}^{+Z(s)} \rho(n, s) = \rho_i(s) \quad (\text{A11})$$

or according to Eqs. (A8) and (A10)

$$\rho(0, s) N(s) = \rho_i(s) \quad (\text{A12})$$

with

$$N(s) = (1-p_+)^{-Z(s)} + (1-p_-)^{-Z(s)} - 1 \quad (\text{A13})$$

Finally, according to Eqs. (A8), (A3), (A10), and (A12)

$$\rho(\pm d, s) = \rho_i(s) \frac{Z(s)!}{d! [Z(s) - d]!} \left(\frac{p_{\pm}}{1-p_{\pm}} \right)^d N(s)^{-1} \quad (\text{A14})$$

as given by Eq. (3) in the text. In particular from Eq. (A14), one gets

$$\sum_{d=0}^{d=Z(s)} \rho(\pm d, s) = \rho_{\pm}(s) (1 - p_{\pm})^{-Z(s)} N(s)^{-1} \quad (\text{A15})$$

which is used in Eq. (8) in the text.

APPENDIX B: s DEPENDENCE OF B

According to Eq. (11b), B varies with s as

$$B(s) = \left[\frac{\beta_+(s)}{\beta_-(s)} \left(\frac{1-p_-}{1-p_+} \right)^{Z(s)} + 1 \right] \left/ \left[1 + \frac{\beta_+(s)}{\beta_-(s)} \right] \right. \left[1 + \left(\frac{1-p_-}{1-p_+} \right)^{Z(s)} - (1-p_-)^{Z(s)} \right] \quad (\text{B1})$$

If a cluster of size s presents the same capture radius for interstitials (+) and vacancies (-), $\beta_+(s)$ and $\beta_-(s)$ exhibit the same s dependence and β_+/β_- may be assumed constant. In the following we write

$$b = \beta_+/\beta_- \quad (\text{B2})$$

$Z(s)$ is the number of trapping centers for defects, at a cluster with s solute atoms. For large s , $Z(s) \propto s^{2/3}$. Since s enters $B(s)$ only through $Z(s)$, we choose Z as new variable. $B(Z)$ may be written as

$$B(Z) = \frac{b(1-p_+)^{-Z} + (1-p_-)^{-Z}}{(1+b)D(Z)} \quad (\text{B3})$$

with

$$D(Z) = (1-p_+)^{-Z} + (1-p_-)^{-Z} - 1 \quad (\text{B4})$$

From Eqs. (B3) and (B4) we get

$$\frac{\partial B}{\partial Z} = \frac{(1-p_+)^{-Z} \ln(1-p_+) [b + (1-b)(1-p_-)^{-Z}] + (1-p_-)^{-Z} \ln(1-p_-) [1 + (1-p_+)^{-Z}(b-1)]}{(1+b)D(Z)^2} \quad (\text{B5})$$

which exhibits the following limits: $Z \rightarrow 0$

$$\frac{\partial B}{\partial Z} \rightarrow \frac{\ln(1-p_+) + b \ln(1-p_-)}{(1+b)D(Z)^2} \quad (\text{B6})$$

$Z \rightarrow \infty$ and $b \neq 1$

$$\frac{\partial B}{\partial Z} \rightarrow \frac{1-b}{1+b} \frac{(1-p_+)^{-Z}(1-p_-)^{-Z} \ln[(1-p_+)/(1-p_-)]}{D^2} \quad (\text{B7})$$

$Z \rightarrow \infty$ and $b = 1$

$$\frac{\partial B}{\partial Z} \rightarrow \frac{(1-p_+)^{-Z} \ln(1-p_+) + (1-p_-)^{-Z} \ln(1-p_-)}{2D^2} \quad (\text{B8})$$

TABLE II. Sign of $\partial B/\partial Z$ as a function of b and p_+/p_- .

b	p_+/p_-		
	< 1	1	> 1
< 1	+	-	-
1	-	-	-
> 1	-	-	+

From Eq. (B6), $\partial B/\partial Z < 0$ for $Z \rightarrow 0$. From Eqs. (B7) and (B8), we find the signs for $\partial B/\partial Z$ as shown in Table II.

APPENDIX C: DEFECTS BALANCE

Under irradiation, the balance equations for vacancies and interstitials are

$$\begin{aligned} \frac{\partial C_v}{\partial t} &= G - KC_i C_v - K_v (C_v - C_v^0) \quad (\text{C1}) \\ \frac{\partial C_i}{\partial t} &= G - KC_i C_v - K_i C_i \end{aligned}$$

where C_v and C_i are the overall concentrations of, respectively, vacancies and interstitials, G the point-defect production rate, K the vacancy-interstitial recombination rate, K_v and K_i the rate of vacancy and interstitial elimination at point-defect sinks and C_v^0 the thermal concentration of vacancies.

At steady state,

$$K_i C_i = K_v (C_v - C_v^0) \quad (C2)$$

K_i and K_v are the product of a geometrical factor by a diffusion coefficient (respectively, D_i and D_v). As-

suming that the sinks are not biased, Eq. (C2) reduces to

$$D_i C_i = D_v (C_v - C_v^0) \quad (C3)$$

It is worth noticing that in this equation, D_i and D_v are effective diffusion coefficients for the point defect in the solid solution, and C_i , C_v , and C_v^0 total defect concentrations (trapped and untrapped at solute atoms). In the text, Eqs. (24) and (25) refer to untrapped point defects only, so that Eq. (25) is valid in the limit of the vanishing solute defect interaction only.

- ¹R. Cauvin and G. Martin, Phys. Rev. B 23, 3333 (1981) (following paper).
- ²K. C. Russell, in *Radiation Effects in Breeder Reactor Structural Materials*, edited by M. L. Bleiberg and J. W. Bennett (American Institute of Mining Engineers, New York, 1977), p. 821.
- ³G. Martin, R. Cauvin, J. L. Bocquet, and A. Barbu, in Proceedings of the International Conference on Irradiation behavior of metallic materials for fast reactor core components, 1979, edited by J. Poirier and J. M. Dupouy (unpublished), p. 75.
- ⁴Y. Adda, M. Beyeler, and G. Brebec, Thin Solid Films 25, 107 (1975).
- ⁵G. Silvestre, A. Silvent, C. Regnard, and G. Sainfort, J. Nucl. Mater. 57, 125 (1975).
- ⁶A. Barbu and A. J. Ardell, Scr. Metall. 9, 1233 (1975).
- ⁷A. Barbu and G. Martin, Scr. Metall. 11, 771 (1977).
- ⁸P. R. Okamoto, A. Taylor, and H. Wiedersich, U.S. ERDA Report No. 75/006 (1975), p. 1188.
- ⁹A. Barbu, in Proceedings of the International Conference on Irradiation behavior of metallic materials for fast reactor core components, 1979, edited by J. Poirier and J. M. Dupouy (unpublished), p. 69.
- ¹⁰Nghi Q. Lam, P. R. Okamoto, H. Wiedersich, and A. Taylor, Metall. Trans. A 9, 1707 (1978).
- ¹¹A. Barbu, CEA Report No. R-4936 (Saclay, France).
- ¹²R. Cauvin and G. Martin, J. Nucl. Mater. 83, 67 (1979).
- ¹³H. R. Brager and F. A. Garner, J. Nucl. Mater. 73, 9 (1978).
- ¹⁴R. K. Williams, J. O. Stiegler, and F. W. Wiffen, ORNL Report T.M. 4500.
- ¹⁵W. Wagner, R. Poerschke, A. Axmann, and D. Schwahn, Phys. Rev. B 21, 3087 (1980).
- ¹⁶P. Wilkes, K. Y. Liou, and R. G. Lott, Radiat. Eff. 29, 249 (1976).
- ¹⁷L. Kaufman, J. S. Watkin, J. H. Gittus, and A. P. Miodownik, Calphad J. 1, 281 (1977).
- ¹⁸A. P. Miodownik and J. S. Watkin, IAEA Report No. SM-236/45 (1979).
- ¹⁹Hisao Yamauchi, J. M. Sanchez, D. de Fontaine, and Ryoichi Kikuchi, in Proceedings of the International Conference on Irradiation behavior of metallic materials for fast reactor core components, 1979, edited by J. Poirier and J. M. Dupouy (unpublished), p. 81.
- ²⁰J. L. Bocquet and G. Martin, J. Nucl. Mater. 83, 186 (1979).
- ²¹J. L. Bocquet (unpublished).
- ²²G. Nocolis and I. Prigogine, *Self organization in non equilibrium systems* (Wiley, New York, 1977), p. 223; H. Haken *Synergetics* (Springer, Berlin, 1978).
- ²³G. Martin, Phys. Rev. B 21, 2122 (1980).
- ²⁴K. Binder, M. M. Kalos, J. L. Lebowitz, and J. Marro, Adv. Colloid Interface Sci., Special Issue on Nucleation Phenomena II 173 (1979); G. Martin, *Solid State Phase Transformations in Metals and Alloys* (Les Editions de Physique, les-Usis, 1980), p. 337.
- ²⁵J. W. Cahn Trans. AIME 242, 166 (1968).
- ²⁶J. S. Langer, Ann. Phys. (N.Y.) 65, 53 (1971).
- ²⁷J. S. Langer and M. Baron, Ann. Phys. (N.Y.) 78, 421 (1973).
- ²⁸J. S. Langer, M. Baron, and H. D. Miller, Phys. Rev. A 11, 1417 (1975).
- ²⁹J. W. Cahn and J. E. Hilliard J. Chem. Phys. 31, 688 (1959).
- ³⁰A. G. Khachaturyan and R. A. Suris, Sov. Phys. Cryst. 13, 63 (1968) [Kristallografiya 13, 83 (1968)].
- ³¹D. de Fontaine, in *Treatise on Solid State Chemistry*, edited by N. B. Hannay (Plenum, New York, 1975), p. 129.
- ³²K. Binder and D. Stauffer, Adv. Phys. 25, 343 (1976).
- ³³O. Penrose, J. L. Lebowitz, J. Marro, M. H. Kalos, and A. Sur, J. Stat. Phys. 19, 243 (1978).
- ³⁴S. I. Maydet and K. C. Russell, J. Nucl. Mater. 64, 101 (1977).
- ³⁵H. Reiss, J. Chem. Phys. 18, 840 (1950).
- ³⁶H. Wiedersich and J. L. Katz, Adv. Colloid Interface Sci., Special Issue on Nucleation Phenomena II, 33 (1979).
- ³⁷K. C. Russell, Acta Metall. 26, 1615 (1978).
- ³⁸K. C. Russell, Acta Metall. 19, 753 (1971).
- ³⁹R. E. Howard and A. B. Lidiard, Rep. Prog. Phys. 27, 161 (1964).
- ⁴⁰A. Barbu, Acta Metall. 28, 499 (1980).
- ⁴¹L. K. Mansur, J. Nucl. Mater. 83, 109 (1979).
- ⁴²G. Martin, Philos. Mag. A 38, 131 (1978).
- ⁴³R. S. Nelson, J. A. Hudson, and D. J. Mazey, J. Nucl. Mater. 44, 318 (1972).
- ⁴⁴C. Abromeit, in Proceedings of the International Conference on Irradiation behavior of metallic materials for fast reactor core components, 1979, edited by J. Poirier and J. M. Dupouy (unpublished), p. 89.