LA-SUB--94-152

Armen G. Khachaturyan

REPORT OF ACTIVITIES AT LANL

Center for Materials Science

March 1, 1994 - July 31 1994

My activity as a B. Matthias Fellow in LANL includes

(a) scientific discussions with LANL personnel

(b) giving seminars in various divisions and groups of LANL

(c) research project with Dr. R. Schwarz at CMS on intermetallic hydrides.

(a) Scientific discussions:

Daily discussions with R. Schwarz on the thermodynamics of coherent open systems.

Dr. A. Saxena, on modeling the martensitic transformations, March 4

Dr. H. Frost, on mechano-optical effect, March 18

Dr. L. Bulaevsky, on the possibility of strain-induced in stability of the Abrikosov lattice in superconductors, March 23

Dr. H. Frost, on Mechano-optical effect, April 4

Dr. R. Blumenfeld, on the strain effects in the transformations, April 8

Dr. A. Saxena, on modeling the martensitic transformations, April 11

Dr. A. Bishop, using the field methods for modeling the shape memory effect, on April 19

Dr. L. Bulaevsky, on the possibility of strain-induced in stability of the Abrikosov lattice in superconductors, May 23

Dr. L. Bulaevsky, on the possibility of strain-induced in stability of the Abrikosov lattice in superconductors, June 15

(b) Seminars

1. Coherent Transformations in Ordering and Decomposing Systems - CMS Seminar (April 8, 1994)
2. Computer Modeling the Structure Transformations - Theory Seminar , T-11, (April 18, 1994)
3. Theory of Pattern Formation in Coherent Transformations- Seminar at the Center of Nonlinear Studies, (July 5, 1994)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

AUG 94

DISCLAIMER

(c) Research project:

THERMODYNAMICS OF COHERENT OPEN SYSTEMS WITH APPLICATIONS TO HYDRIDES: THE PHYSICAL ORIGIN OF HYSTERESIS IN ABSORPTION-DESORPTION ISOTHERMS

The investigators: Armen Khachaturyan and Ricardo Schwarz

The purpose of this project is to resolve an important problem related to a behavior of metal hydrides, *viz.* a physical origin of a strong hysteresis on the pressure-composition isotherms (the plateau pressure during hydrogen absorption is usually several times higher than that during the reverse desorption process). This research which has been started as studying although important but specific problem is ended up by resolving the much more general problem of the behavior of open coherent systems and by formulating the basic concepts of the thermodynamics of an elastically coherent two-phase open system consisting of an interstitial solid solution in the equilibrium with a gas reservoir of solute atoms.

It has been shown that the coherency strain qualitatively changes the character of the transformation from what is expected from conventional thermodynamics for incoherent systems. In particular, the phase rule becomes inapplicable and the 'plateau' on the pressure-composition isotherm does not correspond to a coexisting two-phase state anymore. The coherency strain introduces a non-surmountable macroscopic energy barrier between the transforming phases which prevents the coexistence of the phases and results in a reversible hysteresis in the pressure-composition isotherm. The proposed theory is particularly applicable to metal- hydrogen systems.

We demonstrate, for the first time, that the conventional Gibbs thermodynamics of open elastically coherent systems is "unstable" with respect to even an infinitesimal coherency strain. The coherency strain qualitatively changes the character of the transformation from what is expected from conventional thermodynamics for incoherent systems. Particularly, it blocks the phase transition from the metastable to the stable phase by producing a non-surmountable macroscopic energy barrier between them. This makes the Gibbs phase rules inapplicable (two-phase equilibrium proves to be impossible) and results in a thermodynamically reversible hysteresis on the absorption-desorption isotherms. The latter conclusion has enabled us to explain the hysteresis in hydrides, the phenomenon which cannot be explained in terms of the conventional thermodynamics, as well as to suggest a simple equation for the ratio of the plateau pressures at the absorption and desorption processes.

A key for understanding a non--Gibbsian behavior of coherent interstitial open systems is a role of the coherency strain in the thermodynamics of the phase transformation. Particularly, the strain results in the quadratic dependence of the strain energy on the volume fractions of the coexisting phases and, thus, eliminates the additivity of the thermodynamics. An additivity of the free energies, which is a central part of the Gibbsian thermodynamics, is associated with a usual linear dependence of the free energy on the volume fractions.

The applicability of the proposed theory is far exceeds the particular case of hydrides discussed in this work. With minor modifications, it actually would be also valid for the equilibrium between a decomposing coherent solid solution and melt as well as for the equilibrium between solid reservoir of solute which is in an incoherent contact with the coherent decomposing solid solution.

There are certain indications that the ideas following from this research could be, particularly applied to the problem of imbrittlement of intermetallics.

The results of this work are summarized in manuscripts:

1. The completed manuscript of our paper "On thermodynamics of Open Two-Phase Systems with Coherent Interfaces: Application to Metal-Hydrogen System" written together with Dr. R. Schwarz and submitted to Physical Review Letters. A copy of this paper is attached.
2. Non-finished work with Dr. R. Schwarz "The Structure and Thermodynamics of Ordered Phases in $LaNi_5$-Based Hydrides". After a completion, it is intended to be submitted to Physical Review B

I are going to continue our collaboration with Dr. Schwarz.

Submitted to Physical Review Letters, July 15, 1994

On the Thermodynamics of Open Two-Phase Systems with Coherent Interfaces: Application to Metal-Hydrogen Systems.

R. B. Schwarz and A. G. Khachaturyan †

Center for Materials Science
Los Alamos National Laboratory
Los Alamos, NM 87545

† Department of Materials Science and Engineering
Rutgers University
P.O. Box 909, Piscataway, NJ 08855-0909

The thermodynamic theory for the decomposition of a 'coherent' two-phase open system consisting of an interstitial solid solution in equilibrium with a gas reservoir of solute atoms is developed. It is shown that the coherency strain qualitatively changes the character of the transformation from what is expected from conventional thermodynamics for incoherent systems. In particular, the phase rule becomes inapplicable and the 'plateau' on the pressure-composition isotherm does not correspond to a coexisting two-phase state anymore. The coherency strain introduces a non-surmountable macroscopic energy barrier between the transforming phases which prevents the coexistence of the phases and results in a reversible hysteresis in the pressure-composition isotherm. The proposed theory is particularly applicable to metal- hydrogen systems.

PACS: 64.60.-i, 64.70.Kb, 81.30.-t

It is well known that in two-phase systems with coherent interfaces the transformation-induced strain has a profound effect on the phase transformation thermodynamics, sometimes qualitatively changing its character [1,2]. The elastic strain generated by the interfaces is infinitely long-ranged and thus the strain-induced interaction between the coexisting coherent phases is infinite-ranged as well. This has two nontrivial implications. The first is that the elastic energy contribution to the total free energy of the coherent system is non-additive, i.e., it does not meet the major requirement of the Gibbs thermodynamics. Instead, the total free energy of the coherent system depends non linearly on the volume fractions of the coexisting phases [3]. As a result, the volume fractions of the coexisting coherent phases become internal thermodynamic parameters which are determined from a minimum free energy condition. The second implication is that, in the most general case, the strain energy depends also on the spatial pattern (microstructure) formed by the coherent domains of the coexisting phases and, therefore, the microstructure also becomes a self-adjusting internal thermodynamic parameter [3] . For such a system, the conventional common tangent construction of the additive Gibbs thermodynamics used to find the equilibrium compositions of the coexisting phases ceases to be valid.

The effect of the coherency strain on the thermodynamics of a closed two-phase system with conserved number of atoms has been investigated by Roytburd [1] and Cahn and Larche [2]. These works considered the replacive transformation (decomposition) in an elastically isotropic system producing a two-phase coherent mixture. It was assumed that the crystal lattice parameters of the two phases are different but do not depend on the compositions of these phases. It was shown that for such systems the coherent equilibrium cannot be described by a common tangent rule and that sometimes it even fails to obey the Gibbs phase rule. These results give an important illustration of the above mentioned fact that in systems with coherent interfaces, the strain energy can make the thermodynamics qualitatively different from the conventional Gibbs thermodynamics. However, the model assumed in [1,2] seems to have a limited application. It is inapplicable to most systems decomposing by replacive transformations where the crystal lattice parameters of the coexisting phases are mainly determined by the composition (for example, the γ - γ' transformation in Ni-Al). Furthermore, it has been shown by Lee [4] that in the case where the crystal lattice parameters follow the Vegard law, all the unusual effects expected in coherent thermodynamics [2,3] vanish. These effects can be expected, however, in systems where the misfitting crystal lattice parameters either do not depend on the phase compositions at all, like in the Roytburd and the Cahn and Larche models, or show a very strong deviation from the Vegard law. The lack of such systems seems to be a reason why there is still no reliable experimental confirmation of the strain effects predicted in [1,2].

It will be shown in this Letter that the situation is different for open systems where the solid solution is in a dynamic equilibrium with a reservoir of solute atoms. We demonstrate that unlike the case of replacive transformations in coherent solid solutions with conserved number of atoms, the strain energy has always a drastic effect on the thermodynamic behavior of an open coherent system. These effects should be expected even for an infinitesimal strain energy contribution to the system's free energy. Technologically important examples of such open systems are hydrides in equilibrium with a hydrogen gas reservoir at fixed pressure p and temperature T. Particularly, we demonstrate that for these systems the coherency strain completely eliminates the two phase equilibrium and produces a large thermodynamically reversible hysteresis effect.

Typically, the decomposition of an interstitial solid solution based on a metal or intermetallic matrix results in a formation of two phases characterized by different concentrations of interstitial solute atoms. One phase may be disordered and the other ordered, or both may be ordered. According to classical thermodynamics, such a two-phase system is in thermodynamic equilibrium with the gas of interstitial atoms if the chemical potentials μ_α and μ_β of an interstitial atom the α and β solid phases are equal to the chemical potential $\mu_g(p,T)$ of an atom in the gas phase: $\mu_\alpha(c_\alpha) = \mu_\beta(c_\beta) = \mu_g(p,T)$, where c_α and c_β are concentrations of interstitial atoms in the α and β phases. As long as the concentration of interstitial atoms in the solid is within the two-phase field of the phase diagram, the pressure required to transform the α phase to the β phase is constant. This, in turn, results in a plateau on the pressure-composition isotherm within the two-phase composition range. Measuring the concentration range of the plateau at different temperatures is the main method for the experimental determination of the isobaric temperature-composition, or T-c diagrams of interstitial solutions such as hydrides. It will be shown below that even a small strain introduced by the interstitial atoms drastically changes this picture.

It was shown by Eshelby [5] that the strain energy of a homogeneous elastically isotropic solid solution, where solute atoms are dilatation point defects, is configurationally independent because the strain-induced interaction between the point defects, depending on their mutual position, is zero (Crum's theorem). The Eshelby model, assuming solute atoms to be misfitting elastic spheres coherently imbedded into the parent phase matrix of the volume V, results in the following equation for the strain energy:

$$E_{el} = N v_o \, G \frac{1+\sigma}{1-\sigma} \varepsilon_o^2 \, \bar{c} \, (1 - \bar{c}) \qquad (1)$$

where N is the total number of equivalent lattice sites (in the case of an interstitial solution N is the total number of interstitial sites), $v_o = \frac{V}{N}$, G is the shear modulus, σ is the Poisson ratio, $\varepsilon_o = \frac{da}{adc}$ is the concentration dependence of the crystal lattice parameter, $\bar{c} = \frac{N_1}{N}$, and N_1 is the total number of interstitial solutes in the system. In Eq. (1), the term proportional to $\bar{c}^2$ characterizes the configurationally independent strain-induced interaction which arises through the image forces associated with the free surface of the system. It should be noted that the energy (1) depends on the total number of atoms (through $\bar{c}$) rather than on the local concentrations. Therefore, any regrouping these atoms over the crystal lattice, particularly the one that transforms the homogeneous solid solution of the composition $\bar{c}$ into a two-phase *coherent* mixture of α and β

phases, does not change the total strain energy. It is the same for the homogeneous solid solution as for the two-phase coherent mixture formed by the decomposition of this solution.

With Eq. (1), the Helmholtz free energies (per a lattice site) of the α and β phases in their single phase states, including the strain energy contributions, can be presented as

$$F_\alpha(c) = f_\alpha(c) + A\,c\,(1-c) \tag{2a}$$

and

$$F_\beta(c) = f_\beta(c) + A\,c\,(1-c) \tag{2b}$$

where

$$A = v_0\, G\frac{1+\sigma}{1-\sigma}\,\varepsilon_0^2 \tag{3}$$

We assume that the interstitials do not affect significantly the elastic properties of the matrix and thus A has the same value in both phases. Because the elastic energy of the two-phase coherent system is also described by eq.(1), it can be rewritten in terms of compositions of the phases c_α and c_β and the volume fraction ω of the β phase (more precisely, ω is the relative fraction of the interstitial sites occupied by the β phase). Because the three values, c_α, c_β and ω, are related by the atom conservation equation for interstitial atoms:

$$\omega c_\beta + (1-\omega)\, c_\alpha = \bar{c}\ , \tag{4}$$

the strain energy of the coherent two-phase mixture can be presented as

$$E_{el} = N\, A\, \tilde{c}\,(c_\alpha, c_\beta, \omega)\ [1 - \tilde{c}\,(c_\alpha, c_\beta, \omega)\,] \tag{5}$$

where

$$\tilde{c}\,(c_\alpha, c_\beta, \omega) = \omega c_\beta + (1-\omega)\, c_\alpha \tag{6}$$

In the closed system, the parameters c_α, c_β and ω are not independent since they are related by the atom conservation condition in Eq. (4). This, however, is not the case for the open system where the variables c_α, c_β and ω are independent internal degrees of freedom. Their equilibrium values are determined by a minimum free energy condition.

The free energy of the open two-phase system with variable number of interstitial atoms is the sum of the additive "chemical" part of the free energies, $N(1-\omega)\, f_\alpha(c_\alpha)$ and $N\omega\, f_\beta(c_\beta)$ for the α and β phases, respectively, and the strain energy in Eq. (5). The free energy per a lattice site is thus

$$f(c_\alpha,c_\beta,\omega) = \omega f_\beta(c_\beta) + (1-\omega) f_\alpha(c_\alpha) + A\,\tilde{c}(c_\alpha, c_\beta,\omega)\ [1 - \tilde{c}(c_\alpha, c_\beta,\omega)] \tag{7}$$

Below, without a loss of generality, it is assumed that $c_\beta > c_\alpha$. In an open system which is in dynamic equilibrium with a reservoir of interstitial atoms, the compositions c_α and c_β, as well as the volume fraction ω of the β phase, are all independent variables (internal thermodynamic parameters) which can be found by minimizing the Gibbs free energy

$$g(c_\alpha,c_\beta,\omega) = \omega f_\beta(c_\beta) + (1-\omega) f_\alpha(c_\alpha) + A\ \tilde{c}(c_\alpha, c_\beta,\omega)\ (1 - \tilde{c}(c_\alpha, c_\beta,\omega)) - \mu\,\tilde{c}(c_\alpha, c_\beta,\omega) \tag{8}$$

obtained by adding the term $-\mu\,\tilde{c}(c_\alpha, c_\beta,\omega)$ to Eq. (7). The parameter μ is a Lagrange multiplier which in equilibrium equals the chemical potential of interstitial atoms in the gas phase, $\mu_g(p,T)$. Using Eq. (6), Eq. (8) can be rewritten to show that the specific free energy $g(c_\alpha,c_\beta,\omega)$ has a quadratic dependence on the volume fraction ω:

$$g(c_\alpha,c_\beta,\omega) = \phi_0(c_\alpha) + \phi_1(c_\alpha,c_\beta)\,\omega - \phi_2(c_\alpha,c_\beta)\,\omega^2\ , \tag{9}$$

where

$$\phi_0(c_\alpha) = f_\alpha(c_\alpha) + Ac_\alpha\,(1 - c_\alpha) - \mu\, c_\alpha \tag{10a}$$

$$\phi_1(c_\alpha,c_\beta) = (c_\beta - c_\alpha)\left[\frac{f_\beta(c_\beta) - f_\alpha(c_\alpha)}{c_\beta - c_\alpha} + A\,(1 - 2c_\alpha) - \mu\right] \tag{10b}$$

$$\phi_2(c_\alpha,c_\beta) = A(c_\beta - c_\alpha)^2 > 0 \tag{10c}$$

The quadratic form (9) describes three possible dependencies of g on ω, shown schematically in Fig.1 by curves *a*, *b* and *c*. The curves *a* and c have only one minimum which means that only one stable phase can exist: the α phase for the curve *a* and the β phase for the curve *c*. Curve *b* has two minima, at $\omega = 0$ and at $\omega = 1$, separated by the maximum at $\omega = \omega^*$. For the particular curve *b* shown, the β phase is stable whereas the α phase is metastable. The situation depicted by curve *b* is the most interesting because the phase transition from the metastable α to the stable β phase turns out to be impossible. Indeed, the $\alpha \rightarrow \beta$ transformation requires the formation of the two-phase state with the volume fraction ω^* of the β phase. This, in turn, requires the spontaneous increase in the volume-dependent free energy by the magnitude $Vg(c_\alpha,c_\beta, \omega^*)$. Such an increase is forbidden by the second principle of the thermodynamics. The present situation is quite different from that of the phase transformations in the absence of coherent interfaces and macroscopic strains, where the transformation barriers are microscopic (the formation of critical nuclei) and, as such, can be overcome by thermal fluctuations. Therefore, it follows from the ω dependence of $g(c_\alpha,c_\beta,\omega)$ in Eq. (9), as illustrated by Fig.1, that *two-phase equilibrium in a coherent open system is impossible.* This also means that the phase rule becomes inapplicable to coherent open systems.

Since the free energy barrier between the α and β phase is not surmountable by thermal fluctuations, the $\alpha \rightarrow \beta$ transformation does not starts as long as $\phi_1(c_\alpha,c_\beta,) > 0$ in (9). As μ increases, $\phi_1(c_\alpha,c_\beta,)$ decreases and the α phase looses its stability when $\phi_1(c_\alpha,c_\beta)$ vanishes (ω=0 ceases to be a minimum of $g(c_\alpha,c_\beta,\omega)$). Then, it follows from the definition (10b) and the condition $\phi_1(c_\alpha,c_\beta) = 0$ that

$$\left[\frac{f_\beta(c_\beta) - f_\alpha(c_\alpha)}{c_\beta - c_\alpha} + A\,(1 - 2c_\alpha) - \mu_\alpha(c_\alpha)\right] = 0 \qquad (12)$$

It is taken into consideration in Eq. (12) that $\mu = \mu_\alpha(c_\alpha)$ for the single-phase state of the initial α phase. The chemical potential of the α phase follows from Eq. (2a):

$$\mu_\alpha(c_\alpha) = \frac{\partial F_\alpha}{\partial c}\bigg|_{c=c_\alpha} = \frac{\partial f_\alpha}{\partial c}\bigg|_{c=c_\alpha} + A\,(1 - 2c_\alpha) \qquad (13)$$

Using Eq. (13) to eliminate $\mu_\alpha(c_\alpha)$ from Eq. (12) we obtain the α-phase instability condition in terms of the concentrations only (no strain effects are involved). It reads,

$$\frac{f_\beta(c_\beta) - f_\alpha(c_\alpha)}{c_\beta - c_\alpha} - \frac{\partial f_\alpha(c_\alpha)}{\partial c_\alpha} = 0 \qquad (14)$$

Figure 2a shows the free energies of the α and β phases including the strain contribution (heavy traces) and without the strain contributions (thin traces). From this figure it is clear that Eq.(14) cannot be satisfied if $c_\alpha < c_\alpha^{st}$ because then the left side of Eq. (14) is positive. With increasing c_α, Eq. (14) becomes satisfied when c_α in Fig.2a reaches the point c_α^{st} where the tangent to the curve $f_\alpha(c)$ touches for first time the curve $f_\beta(c)$. Therefore, the stability limit of the α phase, $c_\alpha = c_\alpha^{st}$, is actually determined by the conventional common tangent construction applied to the free energy curves $f_\alpha(c)$ and $f_\beta(c)$ in Fig.2a. In addition to c_α^{st}, this graphical construction also determines the other critical parameters of the transformation: the concentration c_β^{st} of the β phase formed at the beginning of the $\alpha \rightarrow \beta$ transformation and the critical chemical potential $\mu_\alpha(c_\alpha^{st})$, which equals the slope of the tangent line to the curve $F_\alpha(c)$ at the concentration $c = c_\alpha^{st}$. The gas pressure p_1 needed to trigger the $\alpha \rightarrow \beta$ transition is determined by

$$\mu_g(p_1,T) = \mu_\alpha(c_\alpha^{st}) = \frac{\partial f_\alpha}{\partial c}\Big|_{c=c_\alpha^{st}} + A\,(1 - 2c_\alpha^{st}) \qquad (15)$$

which follows from Eq. (13). The composition c_β^{st} of the β phase, formed at the beginning of the $\alpha \rightarrow \beta$ transformation, is not in equilibrium with the external gas reservoir at the pressure p_1 since $\mu_\beta(c_\beta^{st}) < \mu_g(p_1,T) = \mu_\alpha(c_\alpha^{st})$. Indeed, Fig.2a shows that the slopes of the tangent lines at points O_1 and O_2', giving the values of $\mu_\alpha(c_\alpha^{st}) = \mu_g(p_1,T)$ and $\mu_\beta(c_\beta^{st})$, are different. Because $\mu_\beta(c_\beta^{st}) < \mu_\alpha(c_\alpha^{st})$, to establish equilibrium the β phase has to absorb interstitial atoms from the gas phase until its composition reaches c_β^f, where $\mu_\beta(c_\beta^f) = \mu_g(p_1,T) = \mu_\alpha(c_\alpha^{st})$. The composition c_β^f (the point O_2 in Fig.2a) is defined by the condition that the slope of the $F_\beta(c)$ curve at c_β^f equals the slope of $F_\alpha(c)$ at the composition c_α^{st} (the point O_1 in Fig.2a). Therefore, the absorption isotherm should have a plateau at the pressure p_1 within the composition range $c_\alpha^{st} < c < c_\beta^f$ (Fig.2b).

The same line of reasoning gives the graphic algorithm for the desorption isotherm , also illustrated by Fig.2. With decreasing c_β, the $\beta \rightarrow \alpha$ transformation starts at $c = c_\beta^{st}$. The desorption plateau pressure p_2 is determined from the equation

$$\mu_g(p_2,T) = \mu_\beta(c_\beta^{st}) = \frac{\partial F_\beta}{\partial c}\Big|_{c=c_\beta^{st}} = \frac{\partial f_\beta}{\partial c}\Big|_{c=c_\beta^{st}} + A\,(1 - 2c_\beta^{st}) \qquad (16)$$

where $F_\beta(c)$ is given by Eq. (2b). Eq.(16) determines the pressure p_2 for the reverse $\beta \rightarrow \alpha$ transformation. However, the α phase formed as a result of this transformation has the composition c_α^{st} and thus is not equilibrium with the gas phase since at this composition $\mu_\alpha(c_\alpha^{st}) > \mu_g(p_2,T) = \mu_\beta(c_\beta^{st})$ (see Fig.2a). The α phase has to desorb interstitial atoms, reducing its composition from c_α^{st} to c_α^f, until $\mu_\alpha(c_\alpha)$ reaches the equilibrium value, $\mu_\alpha(c_\alpha^f) = \mu_\beta(c_\beta^{st}) = \mu_g(p_2,T)$. Therefore, the desorption isotherm has a plateau at the pressure p_2 within the concentration range $c_\alpha^f < c < c_\beta^{st}$, as shown in Fig.2b.

As follows from the above graphic consideration, the absorption-desorption curves have considerable hysteresis, $\mu_g(p_1,T) - \mu_g(p_2,T) = \mu_\alpha(c_\alpha^{st}) - \mu_\beta(c_\beta^{st})$. The origin of this hysteresis is the coherent strain. From Eqs. (15) and (16), using the equality $\frac{\partial f_\alpha}{\partial c}\Big|_{c=c_\alpha^{st}} = \frac{\partial f_\beta}{\partial c}\Big|_{c=c_\beta^{st}}$ which follows from Fig.2a, we obtain the simple expression

$$\mu_g(p_1,T) - \mu_g(p_2,T) = 2A\,(c_\beta^{st} - c_\alpha^{st}) \tag{17}$$

The chemical potential of interstitial atoms in a diatomic gas is

$$\mu_g(p,T) = \mu(T)_g^o + \frac{1}{2}\,kT\ln\frac{p}{p_o(T)}\ ,$$

where $p_o(T)$ and $\mu(T)_g^o$ are the pressure and chemical potential in the standard state. With it and Eq.(3) we obtain a simple equation for the $\frac{p_1}{p_2}$ ratio characterizing the thermodynamic hysteresis:

$$\ln\frac{p_1}{p_2} = \frac{4\,v_o\,G\,\frac{1+\sigma}{1-\sigma}\,\varepsilon_o^2\,(c_\beta^{st} - c_\alpha^{st})}{kT} \tag{18}$$

The predictions for phase transitions in an open two-phase system with coherent interfaces, derived here, explain certain aspects of the behavior of metal hydrides whose physical origin is still a subject of debates. In particular, they explain the large reversible hysteresis on the pressure-composition isotherms observed in most metal-hydrogen systems, where the plateau pressure during hydrogen absorption is higher than during the reverse desorption process. A general review of this phenomenon was given in [6].

The hysteresis phenomenon in metal hydrides is quite reproducible and separate from the irreversible "activation process" whereby repetitive hydrogenation/dehydrogenation cycles are necessary to activate the alloy into accepting large amount of hydrogen reversibly. During this activation, the hydride decomposes irreversibly into a finely divided powder. Once the activation has been completed, the hysteresis effect is quite reproducible. One of the existing models for the hysteresis [6] postulates that the hysteresis is due to the cyclic plastic deformation involving the repeated generation and annihilation of dislocations. Dislocation plasticity certainly plays an important role in the activation process. It is, however, unlikely that the plasticity alone is responsible for the highly reversible hysteresis phenomenon: this would require the reversible generation and annihilation of the dislocations at the density necessary to accommodate a plastic strain of the order of 15 %.

Another explanation is based on the idea that hydrogen-induced strains are somehow responsible for the hysteresis in hydrides [7]. However, this work only considers the strain energy stored in the local strain field around interstitial point defects. It ignores the macroscopic non-additive volume-dependent strain energy caused by the crystal lattice mismatch between the coherent phases. Besides, as has been noted in [8], a pure elastic strain, by its definition, does not dissipate energy because the stress and strain are always in phase and thus cannot explain the hysteresis loop representing an energy dissipation.

In the present theory, the hysteresis in the pressure-composition diagram of metal-hydrogen systems, and its reproducible character during cycling, follows directly from the thermodynamics for an open two-phase coherent system. The main effect of the strain energy contribution to the free energy is to block the transformation by creating a non-surmountable macroscopic barrier between the initial and final phases. With an increasing applied gas pressure, the transformation barrier eventually vanishes enabling the transformation. The resulting abrupt change in sample volume (proportional to $c_\beta^f - c_\alpha^{st}$) is out of the phase with the applied gas pressure. This necessarily results in energy dissipation and hysteresis. The shape of the p-c hysteresis loop is determined by the system thermodynamics and is thus constant during successive cyclic transformations.

Acknowledgment

The research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. One of the authors (AK) gratefully acknowledges support as the Los Alamos National Laboratory B. Matthias Fellow, 1994.

References

1. A. L.Roytburd, Sov. Phys. -Solid State, **26**, 1229 (1984).
2. J. W. Cahn and F. Larche, Acta Metall. **32**, 1915 (1984).
3. A. G. Khachaturyan, "The Theory of Structural Transformations in Solids" (Wiley & Sons, New York, 1983).
4. J. K. Lee, W. Tao, Acta Metall. et Mater., **84**, 569 (1944)
5. J. D. Eshelby, "Continuum Theory of Defects", in Solid State Physics, edited by ..... (Academic Press, New York, 1956), Vol. 3, p. 79.
6. T. B. Flanagan and J. D. Clewley, J.Less-Common Met. **83**, 127 (1982).
7. V. K. Sinha and W.E. Wallace, J.Less-Common Met. **91**, 239 (1983).

8. T. B. Flanagan and W. A. Oates, " Thermodynamics of Intermetallic Compound-Hydrogen Systems", in Topics in Applied Physics: Hydrogen in Intermetallic Compounds I, edited by L. Schlapbach (Springer-Verlag, New York, 1988), Vol. 63, p. 49.

Figure Captions

Fig. 1 Schematic plot of the dependence of the free energy of the two-phase system on the volume fraction ω of the solute-rich phase. For curve *a*, only the α phase is stable. For curve *b*, the metastable α phase is separated from the stable β phase by a macroscopic energy barrier. For curve *c*, only the β phase is stable.

Fig. 2a. Schematic free energy curves as a function of composition of interstitial atoms for the homogeneous α and β phases of a two-phase system with coherent interfaces. The thin lines show the Helmholtz free energies, $f_\alpha(c)$ and $f_\beta(c)$, without the strain contribution from the interfaces. The bold lines represent the free energies $F_\alpha(c)$ and $F_\beta(c)$ which include the interstitial-induced strain energy; compositions c_α^{st} and c_β^{st} are determined by the common tangent to the $f_\alpha(c)$ and $f_\beta(c)$ curves. The composition c_β^{f} (point O_2) is determined by the condition that the tangent to the curve $F_\beta(c)$ is parallel to the tangent to the curve $F_\alpha(c)$ at the composition c_α^{st} (point O_1). Correspondingly, the composition c_α^{f} is determined by the condition that the tangent to the curve $F_\alpha(c)$ (point O_1') is parallel to the tangent to curve $F_\beta(c)$ at the composition c_β^{st} (point O_2').

Fig. 2b. Chemical potential of the interstitial hydrogen atoms in the gas phase (proportional to the gas pressure) as function of the composition of interstitials in the two-phase solid. The hysteresis is obtained through the absorption-desorption circuit shown by the arrows.

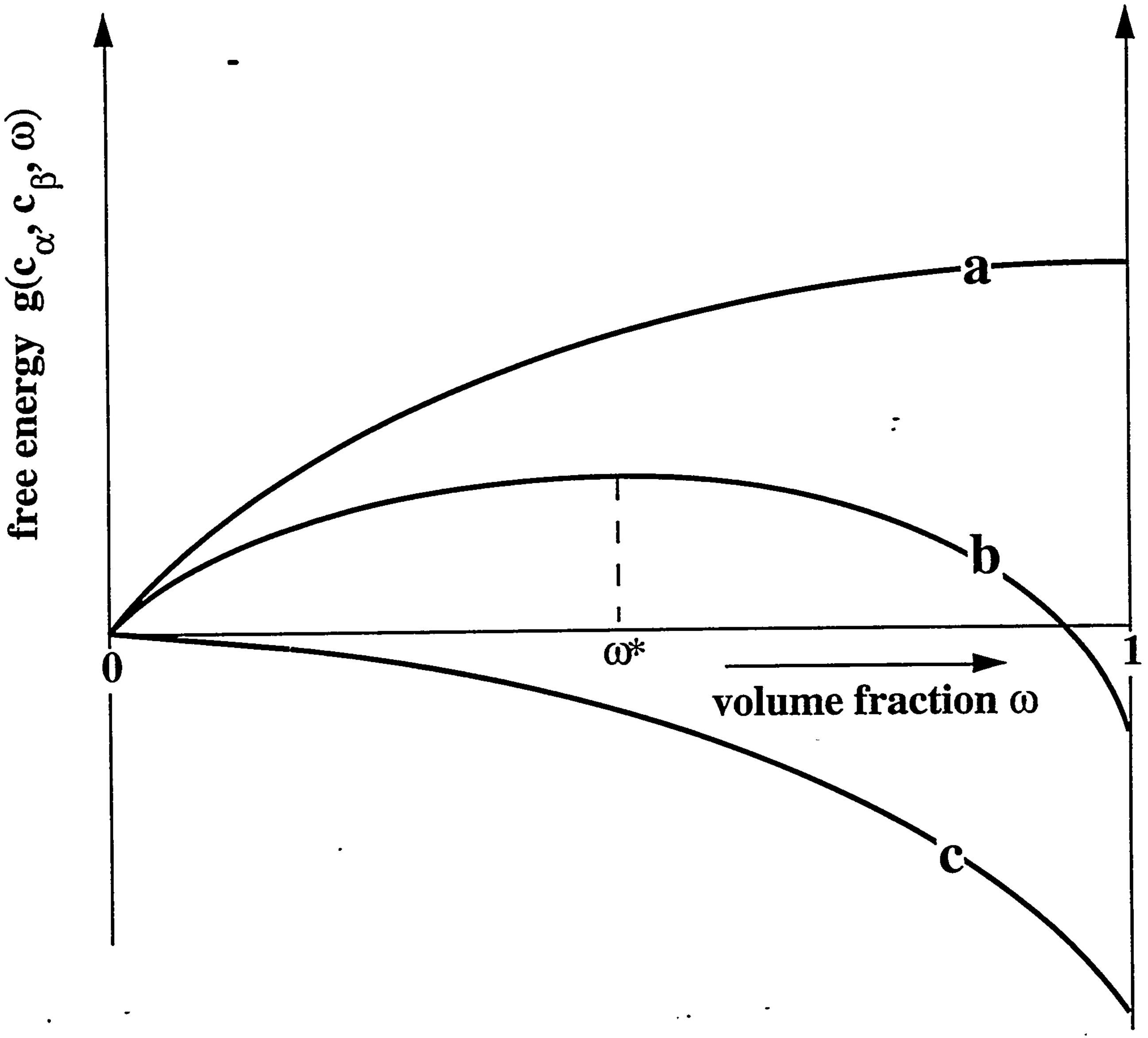

Fig.1

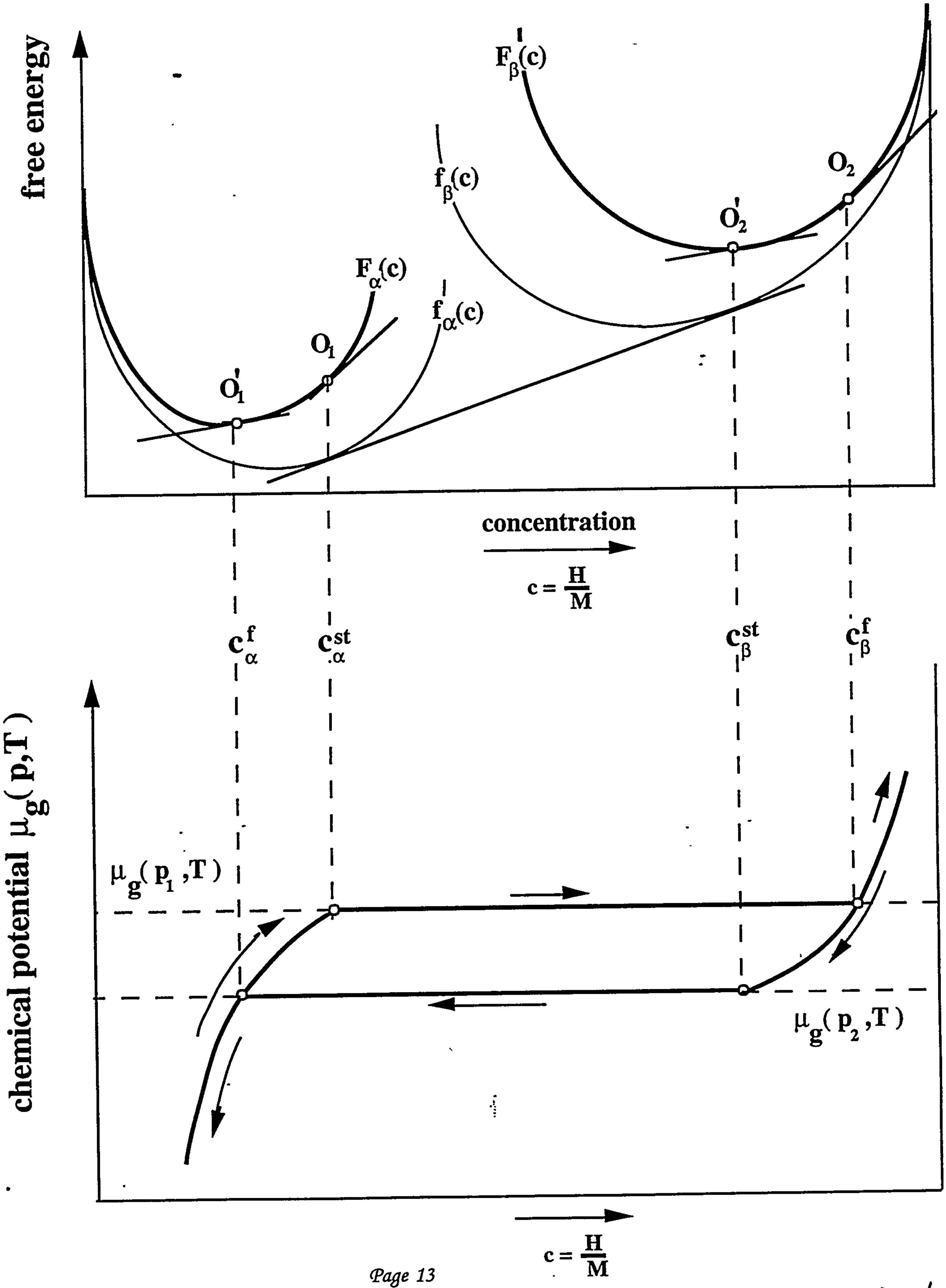
free energy
$F_\beta(c)$
$f_\beta(c)$
O_2
O_2'
$F_\alpha(c)$
$f_\alpha(c)$
O_1
O_1'
concentration
$c = \frac{H}{M}$
c_α^f
c_α^{st}
c_β^{st}
c_β^f
chemical potential $\mu_g(p,T)$
$\mu_g(p_1,T)$
$\mu_g(p_2,T)$
$c = \frac{H}{M}$

Fig. 2 a, b