# Hydrogen in Niobium-Molybdenum Alloys: A Realistic Example of a Random-Field Ising Model

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A theory of metal-hydrogen systems is described which predicts how the phase diagram will change when low concentrations of substitutional impurities are added to the system. Realistic models for $Nb_{0.95}Mo_{0.05}$-H and $Nb_{0.85}Mo_{0.15}$-H systems are developed which are lattice-gas analogs of the random-field Ising model. By Monte Carlo simulation the phase diagrams are obtained and compared with recent experiments.

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During the past decade, there has been considerable interest in the study of random or disordered systems. Both theoretical[1-3] and experimental[4,5] investigations have been directed towards the understanding of the effects of disorder, particularly those caused by impurites on the various physical and chemical properties of magnetic systems. Because of the complex nature of the problem, theoretical studies have, in general, been limited to simple idealized systems. For example, studies have been conducted on Ising models with random interactions between nearest neighbors or with random interactions of infinite range.[1,2] Ising models have also been studied in which the local field conjugate to the spins, rather than the exchange interactions, is random.[3] However, very few theoretical investigations of more realistic and hence more complex systems have been reported.

In this Letter we report the results of our efforts to understand the effects of the randomly distributed substitutional impurity, molybdenum, on the phase diagram of the hydrogen-niobium system. As was originally pointed out by Fenzl and Peisl,[6] this system (which is nonmagnetic) may be considered to be a lattice-gas analog of a random-field Ising model. The interactions between hydrogen atoms and between hydrogen atoms and impurity atoms (the random "field") are calculated by the methods of lattice statics. By the Monte Carlo technique,[7] we have obtained phase diagrams for hydrogen dissolved in $Nb_{0.95}Mo_{0.05}$ and in $Nb_{0.85}Mo_{0.15}$ which are shown to be in reasonable agreement with experiments. Our study illustrates the important role that randomness must play in theories of hydrogen in metals containing impurities.

The phase-change behavior of hydrogen in pure metals is best described by models based on the Horner-Wagner theory[10] in which hydrogen atoms interact with each other directly via electronic interactions, and indirectly via the strain fields produced by the hydrogen atoms in the matrix of the host metal. For example, Fig. 1 shows a comparison between the experimentally determined phase diagram[11] for the H-Nb system and the phase diagram calculated theoretically[12] for this system by the Horner and Wagner approach. Here, the phases $\alpha$ and $\alpha'$ are disordered phases while the $\beta$ phase is an ordered phase. In contrast to the case of hydrogen in pure metals, the behavior of hydrogen in metal alloys is more difficult to model since both the electronic and elastic interactions between hydrogen atoms in an alloy are functions of the local environment surrounding the hydrogen atoms. To account for these changes Futran *et al.*[13] modified the Horner-Wagner model to allow for the presence of two types of metal atoms. In so doing, they assumed that the local configuration of metal atoms surrounding a pair of hydrogen atoms could be approximated by a homogeneous array of metal atoms of a single type with properties intermediate between those of the component metals. When the model was applied to the hydrogen-niobium-vanadium system it was found that the changes in the elastic interactions which occur when vanadium is added substitutionally to the niobium matrix cause a decrease in the $\alpha$-$\alpha'$ critical temperature, $T_c$, as observed in experiments.

When molybdenum is added substitutionally to the hydrogen-niobium system the critical-point temperature also decreases but the effect is much more drastic than when vanadium is added. In fact, the experimental work of Fenzl and Peisl[6] and Matsumoto, Saito, and Fukai[8] has shown that the addition of as little as 5% molybdenum completely erases the $\alpha$-$\alpha'$ transition region. As discussed below in detail, these dramatic changes in the phase diagram can be understood by treating the hydrogen-molybdenum interactions in terms of a random field. The model developed by Futran *et al.*[13] is incapable of describing these dramatic changes in the phase diagram.

The lattice model consists of a body-centered ar-

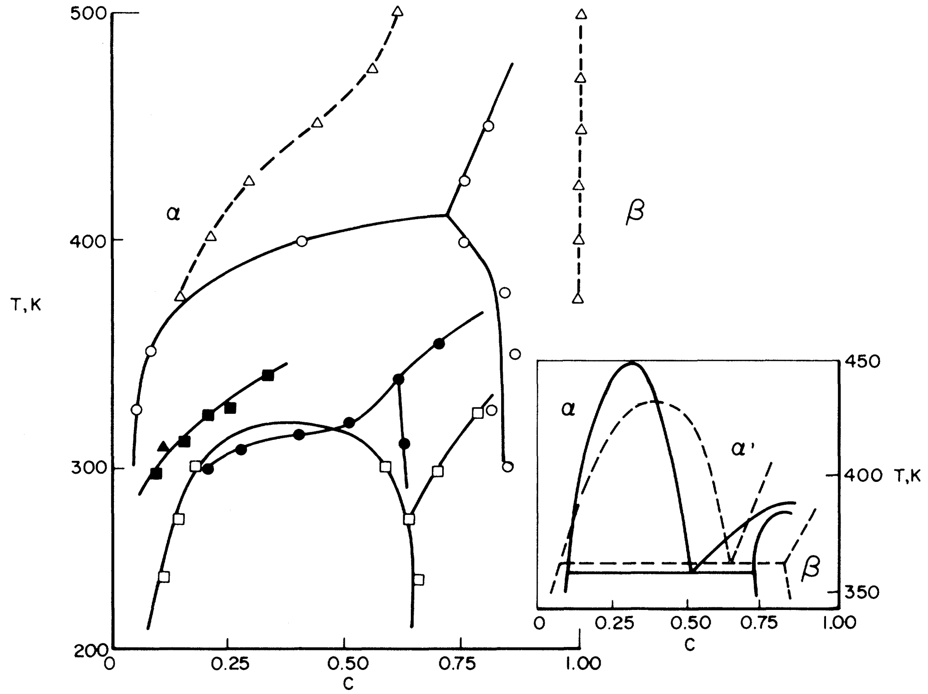

FIG. 1. Comparison of the calculated (open circles) and experimental phase diagrams for $Nb_{0.95}Mo_{0.05}$-H. Experimental points are from Matsumoto, Saito, and Fukai (Ref. 8) (solid squares), Sasaki and Amano (Ref. 9) (solid triangle), and Fenzl and Peisl (Ref. 6) (solid circles). Open triangles are calculated for $Nb_{0.95}Mo_{0.05}$-H without the field and the open squares are calculated for $Nb_{0.85}Mo_{0.15}$-H with the field. The inset shows the experimental (Ref. 11) and calculated (Ref. 12) phase diagram for Nb-H.

ray of $N_L$ metal atoms of which $N_{\mathrm{Mo}}$ are molybdenum and $N_L - N_{\mathrm{Mo}} = N_{\mathrm{Nb}}$ are niobium. The dissolved $N$ hydrogen atoms occupy a fraction of the $N_{\mathrm{H}} = 6N_L$ tetrahedral interstitial sites available to hydrogen atoms. The Hamiltonian describing this hydrogenated alloy contains all possible interatomic potentials between Nb, Mo, and H atoms. When treated in the harmonic approximation, the Hamiltonian separates into a phonon term which is independent of hydrogen concentration (and thus plays no part in the calculation of the phase diagram) and a term which is dependent on hydrogen concentration:

$$H = \sum_{a,c} (W_{ac} + U_{ac}) \tau_a \sigma_c + \tfrac{1}{2} \sum_{a,b} (W_{ab} + U_{ab}) \tau_a \tau_b, \tag{1}$$

where $W_{ab}$ ($W_{ac}$) and $U_{ab}$ ($U_{ac}$) are the elastic and electronic interaction energies, respectively, between a H at interstitial site $a$ and a H (Mo) at interstitial (lattice) site $b$ ($c$). The occupation variable $\tau_a = 1$ or 0 depending upon whether interstitial site $a$ is occupied or unoccupied by a hydrogen atom. Similarly, $\sigma_c = 0$ if lattice site $c$ is occupied by a Nb atom and $= 1$ if it is occupied by a Mo atom.

The elastic interaction energies, $W_{ab}$ and $W_{ac}$ can be calculated from lattice elasticity theory by use of the elastic properties of the metal or alloy in question. Following the discussion of Horner and Wagner,[10] we separate these energies into two parts:

$$W_{ab} = \tilde{W}_{ab} + \Delta W_{ab}; \quad W_{ac} = \tilde{W}_{ac} + \Delta W_{ac}, \tag{2}$$

where $\tilde{W}_{ab}$ and $\tilde{W}_{ac}$ are the interactions in a crystal with periodic boundary conditions and $\Delta W_{ab}$ and $\Delta W_{ac}$ are the corrections necessary for crystals with free surfaces. From lattice statics we find that

$$\tilde{W}_{ab} = -\frac{\Omega}{8\pi^2} \int_{1\mathrm{BZ}} d^3q \sum_{s=1}^{3} \sum_m \sum_n \sum_\mu \psi_\mu^{ma} e_\mu(\vec{q},s) \sum_\nu \psi_\nu^{nb} e_\nu(\vec{q},s) \cos\vec{q} \cdot (\vec{R}^m - \vec{R}^n) / M\omega^2(\vec{q}) \tag{3}$$

where $\Omega =$ volume/(metal atom), $M =$ mass/(metal atom), $\mu$ and $\nu$ are Cartesian coordinates, and $\psi_\mu^{ma}$ is the force in direction $\mu$ between a hydrogen atom at site "$a$" and a metal atom at site "$m$" which has rest position $\vec{R}^m$. The variables $s$, $\omega(\vec{q})$, and $\vec{e}(\vec{q},s)$ are the phonon mode, phonon frequency, and polarization vector for the unloaded (i.e., without hydrogen) lattice. The integration is performed over all wave vectors $\vec{q}$ ($\vec{q} \neq 0$) in the first Brillouin zone. Equation (3) is also used for $W_{ac}$ except that $\psi_\mu^{nb}$ is replaced by $\theta_\mu^{nc}$, the force between a Mo atom at site $c$ and a metal atom (either Nb or Mo) at site $m$. The forces $\psi_\mu^{ma}$ and $\theta_\mu^{nc}$ are determined from measurements of the force-dipole tensor.

The electronic interactions $U_{ab}$ and $U_{ac}$ are extremely difficult to calculate from first principles. Instead, we take a more phenomenological approach and parametrize $U_{ab}$ and $U_{ac}$ from experiment. Following Horner and Wagner,[10] and Futran *et al.*,[13] we approximate $U_{ab}$ as an infinite repulsion out to third neighbors and take $U_{ab} = 0$ beyond that shell. For $U_{ac}$ we use the results of Shirley and Hall[14] who set $U_{ac} = 0.8$ eV for nearest-neighboring Ho-H pairs and $U_{ac} = 0$ beyond that point.

To determine the thermodynamic properties of the system, the terms $\tilde{W}_{ab}$, $\tilde{W}_{ac}$, $U_{ab}$, and $U_{ac}$ are combined into a reference Hamiltonian $H_0$:

$$H_0 = \tfrac{1}{2}\sum_{a,b}(U_{ab} + \tilde{W}_{ab})\tau_a\tau_b + \sum_a h_a\tau_a \qquad (4)$$

where

$$h_a = \sum_c (U_{ac} + \tilde{W}_{ac})\sigma_c \qquad (5)$$

denotes a random field at site $a$. The reference free energy, $A_0$, associated with this Hamiltonian is given by

$$A_0(N,T) = -kT\sum_{\{\sigma_c\}} N^{-1}\ln\left[\sum_{\{\tau_a\}}\exp\left(-\frac{H_0}{kT}\right)\right] \qquad (6)$$

where $k$ is Boltzmann's constant, $T$ is the temperature, and $N$ is the number of field configurations considered. As is customary in cases involving frozen-in disorder, the free energy is evaluated for a given configuration of impurity atoms (field) and then averaged over all impurity configurations. The free-surface corrections to the elastic interactions are of macroscopic range and can be treated (probably exactly) in the mean-field approximation to give the total system free energy

$$A(N,T) = A_0(N,T) + \tfrac{1}{2}(N/N_{\rm H})^2\sum_{a,b}\Delta W_{ab} + (N/N_{\rm H})\sum_{a,c}\Delta W_{ac}. \qquad (7)$$

Since the last term in Eq. (7) is linear in hydrogen concentration, it will appear as a constant in the chemical potential and can be safely ignored. The second term can be evaluated in terms of the trace of the force-dipole tensor, $3P^H$, the bulk modulus, $B$, and the values calculated for $\tilde{W}_{ab}$, by the relation,

$$\sum_{a,b}\Delta W_b = -\frac{N_{\rm H}^2(P^H)^2}{B\Omega} - \sum_{a,b}\tilde{W}_{a,b}. \qquad (8)$$

We use experimental data of Matsumoto, Saito, and Fukai[8] and Powers, Martel, and Woods[15] to obtain $\tilde{W}_{ab}$, $\tilde{W}_{ac}$, $P^H$, and $B$. The Mo concentrations (5%,15%) used in this paper were chosen because of the existence of experimental data for use in calculating the H-H and H-Mo interactions. For details the reader is referred to a later publication.[16]

The probability distribution $P(h_a)$ associated with the random field $h_a$ appearing in Eq. (4) depends on the concentration of the Mo atoms. To determine the distribution function, we first randomly distribute Mo atoms at a given concentration on the bcc lattice and evaluate the sum given in Eq. (5) to obtain $h_a$ for that configuration This procedure is repeated over 50 000 different configurations of Mo atoms randomly distributed on the lattice. The distribution function obtained in this manner is displayed in Fig. 2. The peaks are the result of the very large repulsive interaction which occurs when a hydrogen and a molybdenum are nearest neighbors; the size of each peak is proportional to the probability that the hydrogen atom will have 0, 1, 2, 3, or 4 molybdenum atoms as nearest neighbors. To simplify the random selection of the field values during the Monte Carlo simulation, the

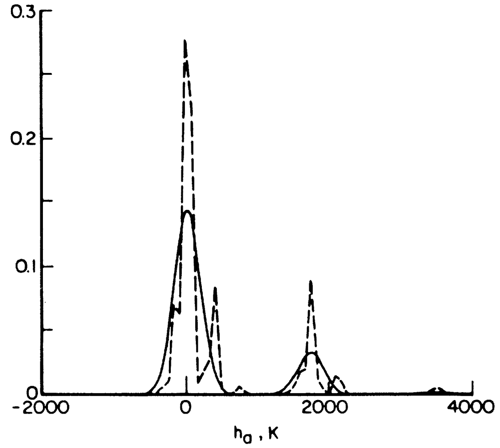

FIG. 2. The probability distribution for the random field, $P(h_a)$. The dashed line is calculated as explained in the text and the solid line represents the fit of this function by a sum of Gaussians.

probability distribution is fitted by a sum of Gaussians with appropriate means and standard deviations. Comparison of the two is shown in Fig. 2.

The free energy for the Nb-Mo-H system is obtained by performing Monte Carlo simulations on a $4 \times 4 \times 2$ unit cell of the bcc lattice which contains 384 tetrahedral interstitial sites. The grand canonical ensemble is used in order to facilitate the search for the order-disorder transition, $\alpha \rightarrow \beta$. In order to generate hydrogen-atom configurations, the standard Monte Carlo simulation techniques[7] are used. For each set of field values $\{h_a\}$, 40 000 hydrogen configurations/chemical potential are considered. This is repeated for twenty different sets of field values, $\{h_a\}$, and a final average of the number of hydrogen atoms, energy, etc., at each chemical potential is calculated.

The phase diagrams calculated theoretically for Nb-H,[12] $Nb_{0.95}Mo_{0.05}$-H, and $Nb_{0.85}Mo_{0.15}$-H are shown in Fig. 1. Also shown in Fig. 1 is a calculated phase diagram for $Nb_{0.95}Mo_{0.05}$-H in which the field energies are set equal to zero; this illustrates the important role played by the random field in the prediction of the phase diagram. The phase diagrams obtained may be compared with the experimentally determined phase diagrams which are also shown in Fig. 1. Fenzl and Peisl[6] found that the $\alpha$-$\alpha'$ coexistence region, which is present in Nb-H (see Fig. 1, inset), completely disappears and the $\alpha$-$\beta$ transition, which is first-order in Nb-H, appears[17] to be second order above a certain temperature (the tricritical point) in $Nb_{0.95}Mo_{0.05}$-H. The $Nb_{0.95}Mo_{0.05}$-H system was also investigated by Matsumoto, Saito, and Fukai[8] and by Sasaki and Amano[9] whose values for the terminal solubility are also shown in Fig. 1. The experimental and theoretical phase diagrams for $Nb_{0.95}Mo_{0.05}$-H agree qualitatively in that both have a first- and second-order $\alpha \rightarrow \beta$ transition separated by a tricritical point. Fenzl and Peisl[6] also list a few data points for $Nb_{0.90}Mo_{0.10}$-H, which indicate that the phase boundaries drop to lower temperatures as the Mo concentration increases in qualitative agreement with the trends we have observed by considering the $Nb_{0.85}Mo_{0.05}$-H system.

In summary, we have developed a theory which predicts how the phase diagram of a metal-hydrogen system will change when low concentrations of substitutional impurities are added to the system. Our model predicts that the addition of as little as 5% Mo to the Nb-H system results in dramatic changes in the phase diagram, in agreement with experimental findings. We conclude that hydrogen-metal systems containing impurities are indeed nonmagnetic experimental realizations of the random-field Ising model.

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