

## Hydrogen in Metallic Alloys as an Example of a Lattice Gas with Random Field and Random Bonds

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We present evidence that hydrogen dissolved in metallic alloys can be considered as a realization of a lattice gas with a random internal field and random bonds. The predictions of this model are in good agreement with experimental phase diagrams and results of diffuse x-ray scattering from microscopic density fluctuations of hydrogen in  $\text{Nb}_{1-x}\text{Mo}_x$  alloys.

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Hydrogen in metals belongs to a class of non-stoichiometric compounds where highly mobile particles move in the periodic potential of a host lattice.<sup>1</sup> The microscopic description of hydrogen in pure metals leads to a Hamiltonian of a deformable lattice gas as proposed by Alefeld.<sup>2</sup> This was further developed theoretically by Wagner and Horner<sup>3</sup> who showed how bulk properties of hydrogen in metals are influenced by boundary conditions at the surface because of long-ranged elastic interactions. As a consequence, the coherent phase transitions depend on the shape of the sample.<sup>4</sup>

In this Letter we show that hydrogen (H) in metallic alloys can be treated as a lattice gas subjected to a random internal field and with random bonds. The disorder which is naturally present in alloys strongly influences the H-H interaction and, thereby, the phase transitions of dissolved hydrogen. The theoretical concept is guided by theories originally developed for disordered magnetic systems or spin-glasses.<sup>5</sup> In this context we may also discuss those particular models which consider only the trapping of hydrogen at defects.<sup>6</sup>

The interaction of hydrogen in metals is usually divided into an electronic and an indirect elastic interaction. The elastic interaction  $W_{ab}$  between hydrogen atoms on interstitial sites  $a$  and  $b$  can be calculated via the lattice Green's function  $G_{ik}^{mn}$  and the forces  $f^{ma}$  and  $f^{nb}$  acting between the hydrogen and the metal atoms on lattice sites  $m$  and  $n$  by the following expression<sup>3</sup>:

$$W_{ab} = \sum_{\substack{i,k \\ m,n}} f_i^{ma} G_{ik}^{mn} f_k^{nb}. \quad (1)$$

In a binary alloy  $A_{1-x}B_x$  the lattice Green's function is subject to fluctuations, at least for microscopic distances  $\mathbf{R}_m - \mathbf{R}_n$ .<sup>7</sup> Moreover, the force  $f^{ma}$  depends on the type of metal atom sitting at  $\mathbf{R}_m$ . The interaction  $W_{ab}$  is therefore no longer translationally invariant in an alloy but depends on the configuration of the surroundings of the  $ab$  pair. Deviations from the configurational average  $\langle W_{ab} \rangle$  lead to random bonds in the lattice-gas Hamiltonian. The screened Coulombic

interaction between the protons, which is also important for the phase transitions, is probably also subject to disorder but it is not possible to formulate it in a simple way.

Perhaps more important than the disturbed interaction is the disorder in the self-energy of the dissolved hydrogen whose elastic part can be obtained from Eq. (1) by setting  $a = b$ . In an alloy this is in general different from site to site depending again on the configuration of the neighboring metal atoms. For example, hydrogen can be trapped at sites near certain atoms with a strong attractive interaction.<sup>6</sup> Deviations of the self-energy from the configurational average  $\langle W_{aa} \rangle$  may be described in the lattice-gas Hamiltonian by a random field,  $h_a$ , to yield the expression

$$H = -\frac{1}{2} \sum_{a \neq b} (\langle W_{ab} \rangle + \Delta W_{ab}) \tau_a \tau_b - \sum_a h_a \tau_a, \quad (2)$$

where  $\tau = 0, 1$  is the occupation number of an interstitial site. In most cases the mobility of the metal atoms is many orders of magnitude lower than the mobility of the protons at the same temperature.<sup>8</sup> The random bonds and the random field can, therefore, be considered as frozen in. From the spatial distribution of the  $A$  and  $B$  atoms one gets the probability distributions  $P_W(\Delta W_{ab})$  and  $P_h(h_a)$ . As one impurity atom interacts with a set of neighboring interstitial sites the random bonds and the random field are correlated within this set. After performing a transformation to spin variables in Eq. (2) we arrive at a Hamiltonian for an Ising model with random bonds and random field. From theories of disordered spin models<sup>5</sup> one knows that the most obvious change is the lowering of the critical temperature with increasing amount of disorder. Inspection of experimental results for hydrogen in alloys provides a general confirmation of this prediction.<sup>9</sup> However, these experiments were not performed with the special considerations described here.

For our experiments we have chosen hydrogen in niobium-molybdenum alloys for several reasons: (i) The phase diagram of hydrogen in pure niobium is well known and its topology bears a great resemblance to that of a real gas-liquid system<sup>10</sup>; (ii) the elements niobium and molybdenum form a continuous series of

solid solutions with a body-centered cubic structure; and (iii) many of their solid-state properties can be found in the literature, e.g., elastic constants,<sup>11</sup> phonon dispersion,<sup>12</sup> and electronic properties,<sup>13</sup> and these are only slightly changed compared to pure niobium if one adds a few atomic percent of molybdenum.

We have determined portions of the phase boundaries of hydrogen in  $\text{Nb}_{1-x}\text{Mo}_x$  for  $x = 0.05$  and  $0.1$  by an x-ray diffraction method.<sup>10</sup> We employed single-crystal samples loaded *in situ* using spot-welded Pd dots to introduce the hydrogen gas.<sup>14</sup> Figure 1 shows that a small amount of Mo in Nb has a dramatic effect on the  $\alpha$ - $\alpha'$  phase transition of the dissolved hydrogen as suggested above.<sup>5,9</sup> An attempt to explain these changes simply by alteration of the elastic interaction fails.<sup>15</sup> The  $\alpha'$ - $\beta$  temperature is only slightly lowered, probably because at high hydrogen concentrations the phase transitions are governed by relatively strong and short-ranged repulsive interactions.

Recently a Monte Carlo calculation<sup>16</sup> demonstrated that our idea of a random field acting on the hydrogen atoms leads to a good agreement between calculated "incoherent" and measured phase diagrams of Fig. 1. In an experiment, however, the ideal incoherent phase diagram can only be approximately determined because a complete coherency-free state is hard to achieve in which the lattices of the two separated phases,  $\alpha$  and  $\alpha'$ , meet at a strain-free incoherent boundary. A physically more crucial quantity for testing our theoretical concept is the compressibility of the lattice gas. Its temperature dependence gives, in addition to the coherent spinodal temperatures, information about the interaction of the dissolved hydrogen. We therefore studied hydrogen density fluctuations by a novel method which employs distortion-induced diffuse x-ray scattering to probe the divergent hydrogen density fluctuations. This may be contrasted with the analogous spinodal determination of Münzing, Stump, and Goeltz who studied temperature-dependent deu-

terium density fluctuations directly in  $\text{NbD}_{0.3}$  using neutron small-angle scattering.<sup>17</sup>

In the present case of distortion-induced fluctuations in the alloy crystals only the so-called microscopic modes,<sup>3</sup> which do not depend on the sample shape and correspond to ordinary long-wavelength density fluctuations in a liquid, contribute to the scattering cross section. The diffuse x-ray scattering cross section close to a Bragg peak (Huang diffuse scattering) is given by<sup>18</sup>

$$d\sigma/d\Omega \propto \langle |c(\mathbf{q})|^2 \rangle |\mathbf{K} \cdot \mathbf{u}(\mathbf{q})|^2. \quad (3)$$

$\mathbf{u}(\mathbf{q})$  is the Fourier transform of the displacement field  $\mathbf{u}(\mathbf{r})$  of a single hydrogen atom,  $\mathbf{K}$  is the scattering vector, and  $\mathbf{q}$  is the reduced wave vector.  $\langle |c(\mathbf{q})|^2 \rangle$  is the Fourier transform of the hydrogen pair correlation  $\langle \tau_a \tau_b \rangle - \langle \tau_a \rangle \langle \tau_b \rangle$ , where the average  $\langle \rangle$  includes a time average as well as an average over the distribution of the random field and random bonds. In the case of a system with frozen disorder the diffuse scattering does not only contain a contribution due to thermal fluctuations but also one due to disorder-induced "frozen" fluctuations. We have estimated this additional contribution to the diffuse scattering under our special conditions of temperature, hydrogen concentration, and strength of disorder. It is less than 10% and therefore we are sure that subtraction of these estimated "frozen" fluctuations introduces, if at all, only a small error. For the thermal part of  $\langle |c(\mathbf{q})|^2 \rangle$  we expect a mean-field behavior for small reduced wave vectors,  $|\mathbf{q}| \ll 2\pi/a_0$ , due to the long-ranged part of the elastic interaction. The temperature dependence is then given by

$$\langle |c(\mathbf{q})|^2 \rangle_{\text{th}} \propto T/[T - T(\mathbf{q})], \quad (4)$$

with  $T(\mathbf{q})$  as the spinodal temperature for the microscopic density-fluctuation modes.<sup>19</sup> Our measurements had to be performed at temperatures above the incoherent phase boundary in order to avoid incoherent precipitation. We obtain  $T_L$  by extrapolating the linear course of  $T/\langle |\tau(\mathbf{q})|^2 \rangle_{\text{th}}$  to zero. Therefore, we cannot decide whether the microscopic density fluctuations actually diverge at  $T_L$  or not. In Fig. 2 the experimentally determined spinodal temperatures for hydrogen in  $\text{Nb}_{0.95}\text{Mo}_{0.05}$ , evaluated by means of Eq. (4), are compared with those in pure niobium. They show a shift towards lower temperatures corresponding to the depressed phase boundaries of Fig. 1. However, in contrast to the measurement and interpretation of phase boundaries, we may now treat properties that are derived for the homogeneous one-phase region.

In a second set of experiments we determined the temperature-dependent scattering cross section in a range of reduced wave vectors from 1 to  $8 \text{ nm}^{-1}$  near the (330) Bragg peak for two different alloys,  $\text{Nb}_{0.99}\text{Mo}_{0.01}$  and  $\text{Nb}_{0.97}\text{Mo}_{0.03}$ , and a hydrogen concen-

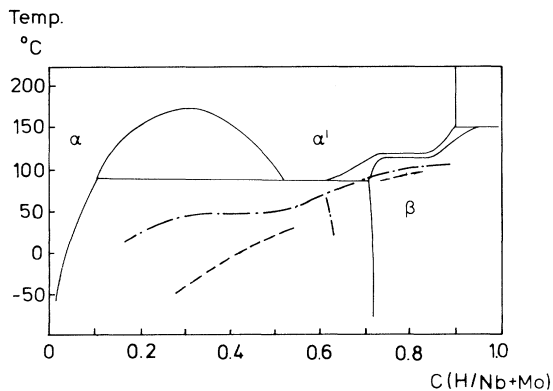


FIG. 1. Phase diagrams of hydrogen in Nb (solid curve, Ref. 10),  $\text{Nb}_{0.95}\text{Mo}_{0.05}$  (dash-dotted curve), and  $\text{Nb}_{0.9}\text{Mo}_{0.1}$  (dashed curve).

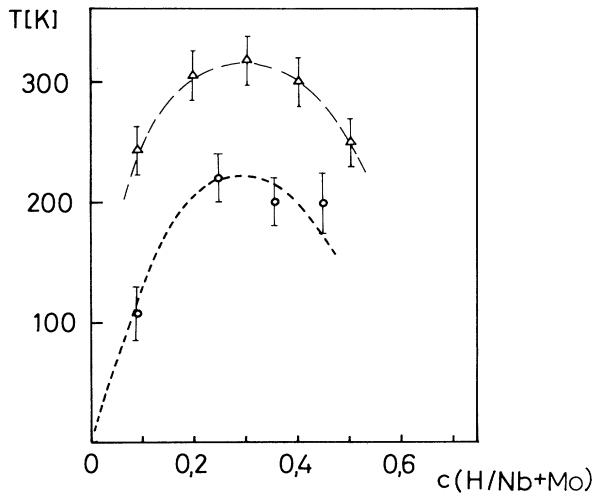


FIG. 2. Spinodal temperatures of microscopic modes for hydrogen in Nb from Ref. 20 (open triangles) and  $\text{Nb}_{0.95}\text{Mo}_{0.05}$  (open circles); dashed curves are guides to the eye.

tration of  $c = 0.31 \text{ H}/(\text{Nb}+\text{Mo})$  corresponding to the critical concentration of the  $\alpha$ - $\alpha'$  transition. In Fig. 3(a) the inverse compressibility calculated from Eq. (3) and with use of the thermodynamic relation<sup>18</sup>

$$K_T^{-1}(q) = c^2 K_B T / V_0 \langle |c(q)|^2 \rangle_{\text{th}},$$

where  $V_0$  is the volume of a metal atom, is plotted versus the temperature for  $|\mathbf{q}| = 1 \text{ nm}^{-1}$ . At this value of  $\mathbf{q}$  the displayed results are nearly identical with the long-wavelength limit of  $K_T^{-1}(\mathbf{q})$ . Figure 3(a) shows the inverse compressibility calculated from a high-temperature series expansion.<sup>21</sup> The calculations assume nearest-neighbor interactions on a bcc lattice and a Gaussian distribution of the random field. The experimental results show the same parallel shift as the theoretical values with increasing disorder, which indicates a decrease in thermal fluctuations due to the random field. For a quantitative comparison a multiplicative scale factor of about 2 must be applied to the ordinate of Fig. 3(b) because the mean occupation number at the critical concentration of our system is considerably smaller than the value of  $\frac{1}{2}$  required by the transformation from spin variables to occupation numbers. In the  $\text{Nb}_{0.97}\text{Mo}_{0.03}$  alloy the spinodal temperature  $T_L$  is changed by about  $-15\%$  relative to pure Nb. The same relative change is obtained in the lattice-gas model on the assumption of a Gaussian-distributed random field with a standard deviation  $\sigma = 26 \text{ meV}$ .

Actually the random field is created by the repulsive interaction of Mo and H in Nb. Computer calculations showed that this leads to a random field which can be described by several Gaussian distributions.<sup>16</sup> The

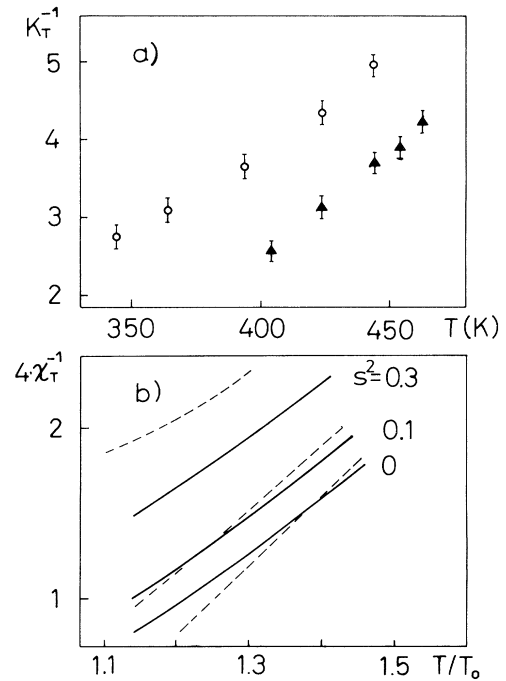


FIG. 3. (a) Inverse compressibility for microscopic hydrogen density-fluctuation modes in  $\text{Nb}_{0.99}\text{Mo}_{0.01}$  (filled triangles) and  $\text{Nb}_{0.97}\text{Mo}_{0.03}$  (open circles). Dimensionless units have been chosen for comparison with (b); to convert to normal units ( $\text{eV}/\text{\AA}^3$ ) multiply by 0.15. (b) Inverse susceptibility of an Ising model with random field after Ref. 21; the standard deviation of the Gaussian distribution is denoted by  $s = \sigma/kT_c$  and both axes are scaled by the critical temperature of the pure system. Indicated as well (dashed curve) is the inverse susceptibility of an Ising model with infinite-ranged interaction after Ref. 22.

average of their standard deviations weighted with the peak height gives a value of  $\bar{\sigma} = 17 \text{ meV}$ . This is of the same order of magnitude as the above value  $\sigma$  and can be eventually improved by including the effect of random bonds. We have also included in Fig. 3(b) the results of an exact calculation of  $\chi_T^{-1}$  under the assumption of infinite-ranged (constant) interactions normalized per spin.<sup>22</sup> This calculation represents the other extreme from the nearest-neighbor case and our results should in principle lie within the range covered by these two extremes.

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