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Phase separation in amorphous metal hydrides: A Stoner-type criterion

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The existence of dissociation plateaus in the pressure-composition isotherms for hydrogen absorption in amorphous metals is shown to depend on the degree of configurational disorder in the host lattice. Within a mean-field approximation for the attractive elastic hydrogen-hydrogen interaction, the Stoner-type condition $-an(E_0) \geq 1$ is derived for the existence of a positive critical temperature T_c [a is a measure of the strength of the effective hydrogen-hydrogen interaction and $n(E_0)$ is the maximum of the symmetric density-of-sites function $n(E)$ which describes the spread in the energy of the sites which can be occupied by hydrogen atoms]. Analytical expressions for T_c are derived for a square and a double-square density-of-sites function. These simple models for $n(E)$ are used to reproduce experimental results on crystalline and amorphous nickel-zirconium hydrides.

I. INTRODUCTION

It has recently been shown that amorphous metals can absorb relatively large amounts of hydrogen at moderate pressures.[1-3] To our knowledge the pressure-composition isotherms of all the amorphous alloys investigated so far do not exhibit plateaus. This is a striking result as for some of these alloys it is known that the pressure-composition isotherms for hydrogen absorption in the *crystallized* alloys do have plateaus. A good example is shown in Fig. 1 for the case of $Ni_{50}Zr_{50}$. At 374 K the isotherm measured by Libowitz *et al.*[4] on crystalline $Ni_{50}Zr_{50}$ has a plateau at ~0.7 mm Hg while the isotherms of the amorphous substance[1] are very steep in the concentration range between $c = 0.5$ and 1.0. The purpose of the present work is to show that the absence of phase separation in amorphous metal hydrides is related to the disorder in atomic positions inherent to these materials.

II. THEORETICAL MODEL

As a consequence of configurational disorder the energy E of the interstitial sites which can be occupied by a hydrogen atom varies from site to site. The probability to find a site with an energy between E and $E + dE$ is given by $n(E)dE$, where $n(E)$ is the *density-of-sites* function of the metallic glass under consideration. The density-of-sites function is often assumed to be of Gaussian form.[5] For the present discussion we shall, however, only require that

$$\int_{-\infty}^{+\infty} n(E)dE = 1 , \tag{1}$$

which implies that there is on the average one site per host-metal atom which can be occupied by a hydrogen atom.

The concentration $c = [\mathrm{H}]/[M]$ of hydrogen in the alloy is given by the implicit relation

$$\int_{-\infty}^{+\infty} n(E)x(E,\mu,T,c)dE = c , \tag{2}$$

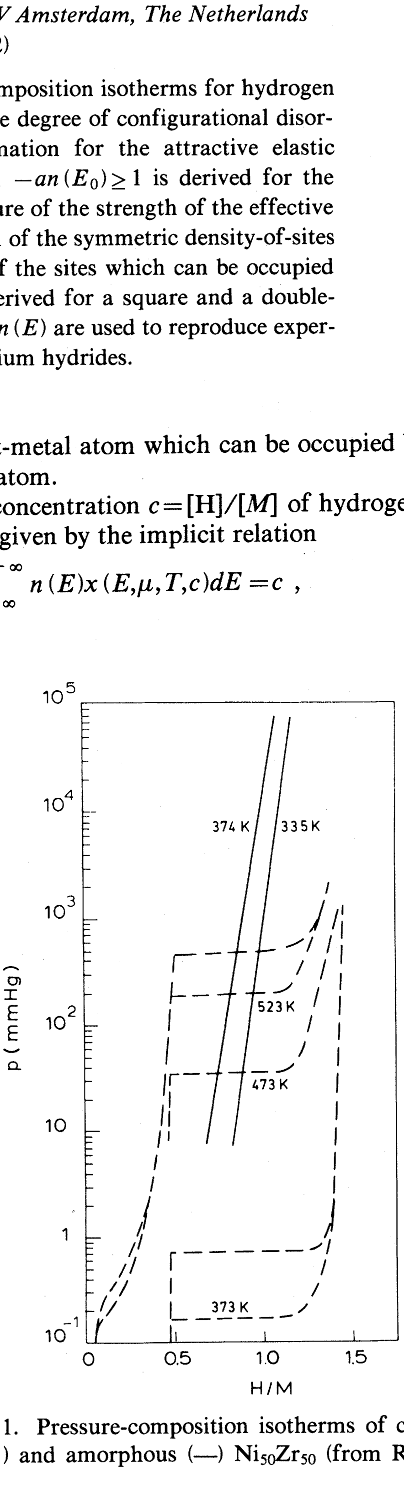

FIG. 1. Pressure-composition isotherms of crystalline (— — —) and amorphous (—) $Ni_{50}Zr_{50}$ (from Refs. 1, 2, and 4).

where $x(E,\mu,T,c)$ is the partial concentration of hydrogen occupying sites of potential energy E at temperature T when the sample is in contact with hydrogen gas at pressure p. At equilibrium the chemical potential μ of hydrogen dissolved in a metal is related to the chemical potential μ_{H_2} of gaseous hydrogen by means of the relation

$$\mu = \tfrac{1}{2}\mu_{\mathrm{H}_2} = \tfrac{1}{2}kT\ln(p/p_0')\ , \tag{3}$$

where p_0' varies as $T^{7/2}$ (see Ref. 6).

In the absence of hydrogen-hydrogen interaction $x(E,\mu,T)$ is simply given by the Fermi-Dirac distribution function since each site can only be occupied by one hydrogen atom. In the presence of a hydrogen-hydrogen interaction the partial hydrogen concentration x is readily obtained from the following expression for the chemical potential:

$$\mu = kT\ln\left[\frac{x}{1-x}\right] + (E-E_b) + \Delta\mu_{\mathrm{el}} + \Delta\mu_{\mathrm{elast}} + \mu_{\mathrm{vib}}\ , \tag{4}$$

where E_b is half the binding energy of the H_2 molecule. $\Delta\mu_{\mathrm{el}}$ and $\Delta\mu_{\mathrm{elast}}$ are the "electronic" and "elastic" contributions to the chemical potential and μ_{vib} is the contribution of the vibration of hydrogen in the host lattice. In a good approximation it can be assumed that μ_{vib} is independent of concentration. Furthermore, its temperature dependence is almost the same as that of p_0' in Eq. (3). For the equilibrium hydrogen-gas pressure we thus obtain

$$kT\ln\left[\frac{p}{p_0}\right] = 2kT\ln\left[\frac{x}{1-x}\right] + 2(E-E_b) + 2(\Delta\mu_{\mathrm{el}} + \Delta\mu_{\mathrm{elast}})\ , \tag{5}$$

where p_0 is now an effective pressure which is essentially constant in the range of temperature $T \lesssim T_{\mathrm{recryst}}$.

In a first approximation the excess electronic contribution $\Delta\mu_{\mathrm{el}}$ is given by

$$\Delta\mu_{\mathrm{el}} = \mu_{\mathrm{el}}(c) - \mu_{\mathrm{el}}\ \ (c=0) \tag{6}$$

with

$$\mu_{\mathrm{el}}(c) = \frac{\int EN(E)f(E,c,T)dE}{\int N(E)f(E,c,T)dE}\ , \tag{7}$$

where $f(E,c,T)$ is the Fermi-Dirac distribution function for the electrons in a metal-hydrogen system with $[\mathrm{H}]/[M]=c$. Since in this work we are primarily interested in the effect of configurational disorder on pressure-composition isotherms we shall evaluate Eq. (7) to lowest order in the total concentration[7] and neglect the weak temperature dependence in the Fermi-Dirac distribution function. One then obtains

$$\Delta\mu_{\mathrm{el}} = a_{\mathrm{el}}c = \frac{\alpha}{N(E_F)}c\ , \tag{8}$$

where $N(E_F)$ is the electronic density of states at the Fermi energy E_F and α is the fraction of electrons per added hydrogen which fill states at E_F.[8–10]

On the basis of existing theories[11–13] of the elastic interaction between two hydrogens (or defects in general) one finds that

$$\Delta\mu_{\mathrm{elast}} = a_{\mathrm{elast}}c = -\frac{P^2}{\Omega B}\frac{2}{3}\left[\frac{1-2\nu}{1-\nu}\right]c\ , \tag{9}$$

where Ω is the atomic volume, P the trace of the dipole moment tensor, B the bulk modulus, and ν the Poisson ratio of the material under consideration. From thermodynamical considerations it is known that $B>0$ and that $0 \le \nu < \frac{1}{2}$. Therefore, a_{elast} is always negative if the hydrogen-hydrogen interaction is mediated by the dilation of the host-metal matrix. This attractive interaction is responsible for the existence of miscibility gaps in many *crystalline* metal hydrides. Since amorphous metals do not contain dislocations it is reasonable to assume that Eq. (9) will also hold for the amorphous metal hydrides considered in this work. In the remaining part of this paper we shall therefore discuss the properties of the following version of Eq. 5:

$$\ln\left[\frac{p}{p_0}\right] = 2\ln\left[\frac{x}{1-x}\right] + \frac{2}{kT}(E-E_b+ac) \tag{10}$$

with

$$a = a_{\mathrm{el}} + a_{\mathrm{elast}}\ . \tag{11}$$

For *crystalline* materials the density-of-sites function $n(E)$ is a δ function (a set of δ functions in the general case), and according to Eq. (2) there is no difference between partial and total concentrations x and c. Equation (1) reduces then to a well-known expression first derived by Lacher[14] to describe the absorption of hydrogen in palladium.

For *amorphous* materials the difference between partial and total concentration is essential. The entropy term $\ln[x/(1-x)]$ depends only on the occupation of the sites of a given energy. The hydrogen-hydrogen interaction term ac, on the other hand, depends on the total concentration since it is assumed to arise (i) from the dilation of the metal matrix by *all* hydrogen atoms present in the sample and (ii) from a shift of the Fermi energy of the electrons.

The distribution function $x(E,\mu,T,c)$ corresponding to Eq. (10) is still of the Fermi-Dirac form, i.e.,

$$x(E,\mu,T,c)=\frac{1}{e^z+1} \tag{12}$$

with $z=(E-E_b+ac-\mu)/kT$, but the effective chemical potential $\mu_F=E_b+\mu-ac$ is now explicitly concentration dependent. The pressure-composition isotherms corresponding to Eq. (5) are given by the condition

$$c=\int_{-\infty}^{+\infty} n(E)\frac{1}{e^z+1}dE\ . \tag{13}$$

The condition for the existence of plateaus in the pressure-composition isotherms is that the critical temperature T_c must be positive. The critical temperature is determined by the two conditions[6]

$$\left.\frac{\partial\mu}{\partial c}\right|_{c_c,T_c,p_c}=0 \tag{14}$$

and

$$\left.\frac{\partial^2\mu}{\partial c^2}\right|_{c_c,T_c,p_c}=0\ , \tag{15}$$

where c_c, T_c, and p_c are the critical concentration, temperature, and pressure. These two relations lead to the conditions

$$T_c=-\frac{a}{2k}\int_{-\infty}^{+\infty} n(E)\frac{1}{1+\cosh z_c}dE \tag{16}$$

and

$$0=\int_{-\infty}^{+\infty} n(E)\frac{\sinh z_c}{(1+\cosh z_c)^2}dE \tag{17}$$

with

$$z_c=(E-\mu_F^c)/(kT_c)\ , \tag{18}$$

where μ_F^c is the chemical potential μ_F evaluated at the critical point.

For the case of a simply peaked density-of-sites curve $n(E)$ which is symmetric with respect to an energy E_0 the integral in Eq. (17) vanishes only if

$$\mu_F^c\equiv E_b+\mu_c-ac=E_0\ , \tag{19}$$

i.e., if the function

$$\sinh z_c/(1+\cosh z_c)^2$$

is antisymmetric with respect to $E=E_0$. Introducing Eq. (19) in Eqs. (13) and (16) we obtain

$$c_c=\tfrac{1}{2} \tag{20}$$

and

$$T_c=-\frac{a}{2k}\int_{-\infty}^{+\infty} n(E)\frac{1}{1+\cosh[(E-E_0)/kT_c]}dE\ . \tag{21}$$

This implicit equation for T_c leads to the following conclusions:

(i) The critical temperature for hydrogen in an *amorphous* material is always lower than the T_c of the pressure-composition isotherms of a *crystalline* material with the same hydrogen-hydrogen interaction strength a. This follows from the fact that the integrand in Eq. (21) is always smaller than $\frac{1}{2}$ and that for crystalline materials T_c (crystalline) $=-a/(4k)$.

(ii) A positive critical temperature T_c is only possible if the hydrogen-hydrogen interaction is sufficiently attractive. In the limit $T_c\rightarrow 0$, Eq. (21) reduces to $a=-1/n(E_0)$, and consequently $T_c\geq 0$ requires that

$$-an(E_0)\geq 1\ . \tag{22}$$

This condition is analogous to the well-known Stoner[15,16] condition $IN(E_F)\geq 1$ for the existence of ferromagnetism. The strength $(-a)$ of the hydrogen-hydrogen interaction plays the same role as the exchange interaction parameter I. As mentioned earlier the density of sites, $n(E)$, is the analog of the density of states, $N(E)$, for electrons.

In crystallized alloys the density-of-sites function is not necessarily a δ function. The width of $n(E)$ will, however, be much smaller than in amorphous materials. The experimental observation of the absence of plateaus in amorphous substances indicates, therefore, that the width $2\Delta\approx 1/n(E_0)$ of $n(E)$ is such that $2\Delta\gtrsim -a$. In crystallized substances $2\Delta\ll -a$ (we assume here that $a<0$). Considering that in crystalline hydrogen absorbers[17] such as Pd, Nb, V, and Ta, $a\approx -0.2$ eV, one expects that $2\Delta\gtrsim 0.2$ eV in amorphous materials. An experimental confirmation of this point will be given in the next section.

The aforementioned conclusions are also valid for a general form of the density-of-sites function. For a general $n(E)$ the value of μ_F^c which satisfies Eq. (17) is, however, not simply related to the characteristic form of the density of sites. Furthermore, for a multipeaked function Eq. (17) can be satisfied by several different values of μ_F^c. The Stoner-type condition (22) has then to be written

$$-an(E=\mu_F^c)\geq 1\ . \tag{23}$$

The case of a double-peaked density-of-sites function shall be considered in Sec. III B.

III. SIMPLE MODELS

A. The square density-of-sites model

In order to obtain analytical expressions for the pressure-composition isotherms of an amorphous substance we consider here the case of a square density-of-sites curve such that

$$\begin{aligned} &n(E)=1/2\Delta \quad \text{for } E_0-\Delta \le E \le E_0+\Delta \\ &n(E)=0 \quad \text{otherwise} . \end{aligned} \tag{24}$$

The total hydrogen concentraction c is then given by

$$c=\frac{1}{2\Delta}\int_{E_0-\Delta}^{E_0+\Delta}\frac{1}{e^z+1}dE , \tag{25}$$

from which it follows that

$$\frac{1}{2}\ln\left[\frac{p}{p_0}\right]=\frac{E_0-E_b+ac-\Delta}{kT}+\ln\left[\frac{e^{2\Delta c/kT}-1}{1-\exp[2\Delta(c-1)/kT]}\right] . \tag{26}$$

Pressure-composition isotherms corresponding to various values of the width 2Δ of the density-of-sites curve are given in Figs. 2(a)–(2c). For $\Delta=0$, Eq. (26) reduces to Lacher's expression

$$\frac{1}{2}\ln\left[\frac{p}{p_0}\right]=\frac{E_0-E_b+ac}{kT}+\ln\left[\frac{c}{1-c}\right] . \tag{27}$$

For $\Delta<-a/2$ the isotherms exhibit plateaus in agreement with the criterion for $T_c\ge 0$ given in Eq. (22). The critical temperature decreases with increasing disorder according to

$$\frac{T_c}{T_c(\Delta=0)}=2\frac{\delta}{\ln[(1+\delta)/(1-\delta)]} , \tag{28}$$

where $\delta=-2\Delta/a$. This function is indicated in Fig. 3. At low values of δ, T_c varies quadratically with the disorder Δ. Above $\delta=1$ the critical point does not exist anymore and the isotherms do not exhibit plateaus. In this high-disorder regime the isotherms resemble those of a crystalline substance ($\Delta=0$) with a *repulsive* hydrogen-hydrogen interaction ($a>0$), i.e., the isotherms flatten with *increasing* temperature [see Fig. 2(c)].

B. The double-square density-of-sites model

Amorphous materials are alloys of two or several elements. Even in crystallized form these alloys will

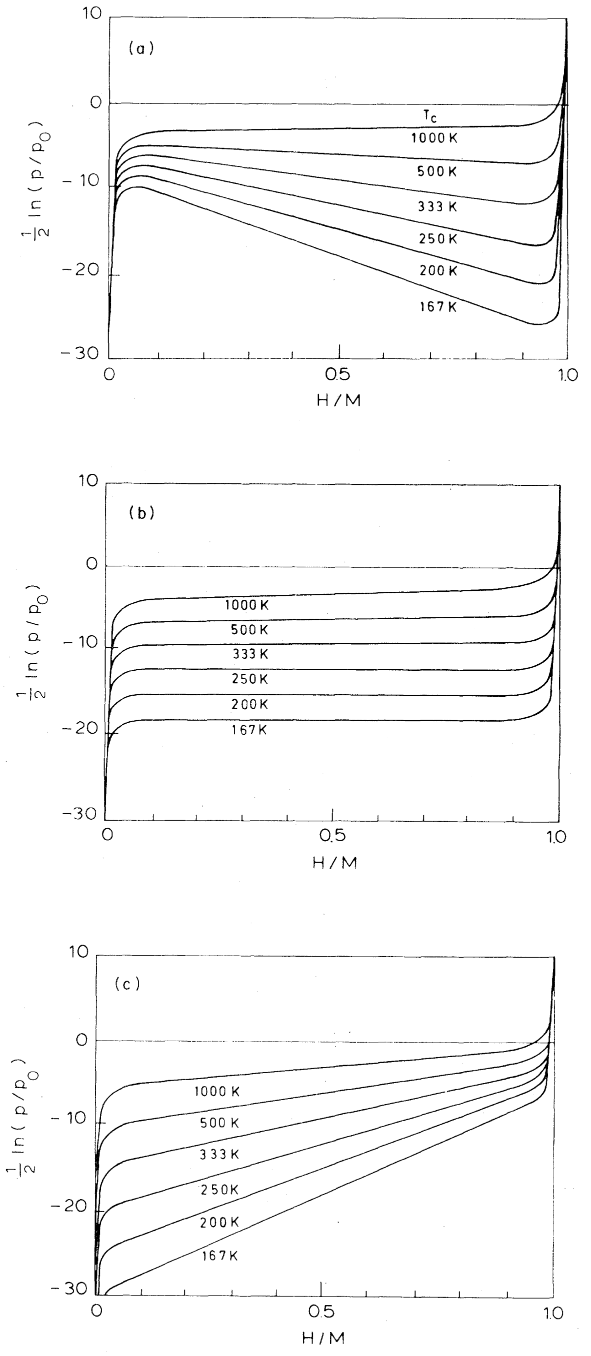

FIG. 2. Pressure-composition isotherms for hydrogen absorption in (a) a perfectly crystallized substance with $\Delta=0$, (b) an amorphous substance with $\Delta=0.172$ eV (2000 K), and (c) an amorphous substance with $\Delta=0.345$ eV (4000 K). For the three cases $E_0-E_b=-0.086$ eV (-1000 K) and $a=-0.345$ eV (-4000 K). In curve (a) the critical temperature is $T_c=1000$ K while in (b) $T_c=0$ K since $2\Delta=-a$. For clarity the plateaus which would result from the application of Maxwell's construction to the isotherms are not shown in Fig. 2(a).

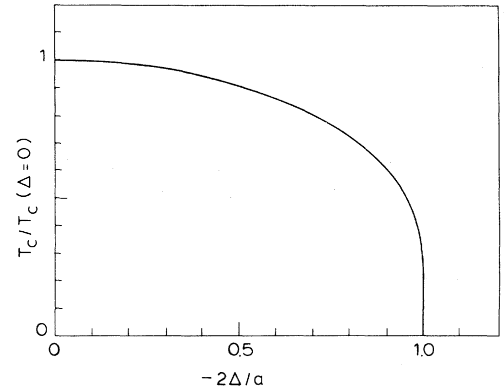

FIG. 3. Critical temperature as a function of the "disorder" parameter $-2\Delta/a$. T_c is normalized to the perfect crystal value $T_c(\Delta=0)=-a/4k$.

in general contain several possible interstitial sites which can be occupied by hydrogen. The density-of-sites function $n(E)$ of the crystallized alloys consists then of various δ functions. In the amorphous state these δ functions are smeared out and may even overlap each other. A simple model which can be used to discuss the isotherms of many-sites systems is the double-square density-of-sites model shown in Fig. 4.

The isotherms corresponding to this model are obtained by integration of Eq. (13). This leads to

$$\tfrac{1}{2}\ln\left[\frac{p}{p_0}\right]=\frac{E_0-E_b+ac}{kT}+\ln\left[\frac{K}{L}\right] \tag{29}$$

with

$$K=e^{-2\Delta/kT}-\exp[2\Delta(2c-1)/kT] \tag{30a}$$

and

$$L=M\cosh\left[\frac{S}{kT}\right]-\left[M^2\cosh^2\left[\frac{S}{kT}\right]-K\{1-\exp[4\Delta(c-1)/kT]\}\right]^{1/2}, \tag{30b}$$

where

$$M=\exp[\Delta(4c-3)/kT]-e^{-\Delta/kT}\,. \tag{30c}$$

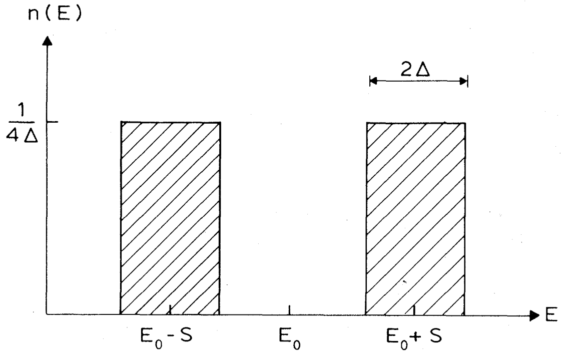

FIG. 4. $n(E)$ for the double-square density-of-sites model.

For a perfectly crystallized substance $\Delta=0$ and the isotherms have two plateaus as shown in Fig. 5(a). There are two critical points and the critical concentrations are $c_1\cong0.25$ and $c_2\cong0.75$. With increasing disorder the two plateaus disappear and one obtains the situation shown in Fig. 5(b). As $\Delta>S$ the two-square density of sites centered at E_0+S and E_0-S overlap each other and $n(E)$ now has a maximum at E_0 such that $n(E_0)=1/2\Delta$. From the condition (22) it follows that $T_c\geq0$ if $2\Delta<-a$. This is the same criterion as for the single-square density-of-sites model. The width of the plateaus is, however, drastically reduced as can be seen by comparing Fig. 2(b) with Fig. 5(b).

The dependence of T_c on disorder for metal-hydrogen systems with $S=0.1293$ eV ($=1500$ K) is indicated in Fig. 6 for various values of the hydrogen-hydrogen interaction parameter a. In region II the system has two different critical concentrations while in the rest of the diagram (region I) there is only one critical point.

The dependence of T_c on the parameters Δ, S, and a cannot be given analytically. However, some special points of the curves in Fig. 6 are determined by simple general relations. For example, the separation line between the one-plateau and two-plateau regions at $\Delta=0$ is determined by the conditions

$$-a/S=4.6685 \tag{31a}$$

and

$$kT_c^0/S=0.6480\,. \tag{31b}$$

For $-a>-a_0>0$ (weak attractive hydrogen-hydrogen interaction) kT_c is approximately equal to $-a/8$. For $a<a_0$ (strong attractive interaction) the critical temperature is determined by the condition

$$1+\cosh\left[\frac{S}{kT_c}\right]+\frac{a}{2kT_c}=0\,. \tag{32}$$

For $\Delta<S$, T_c vanishes for $a=-4\Delta$, while for

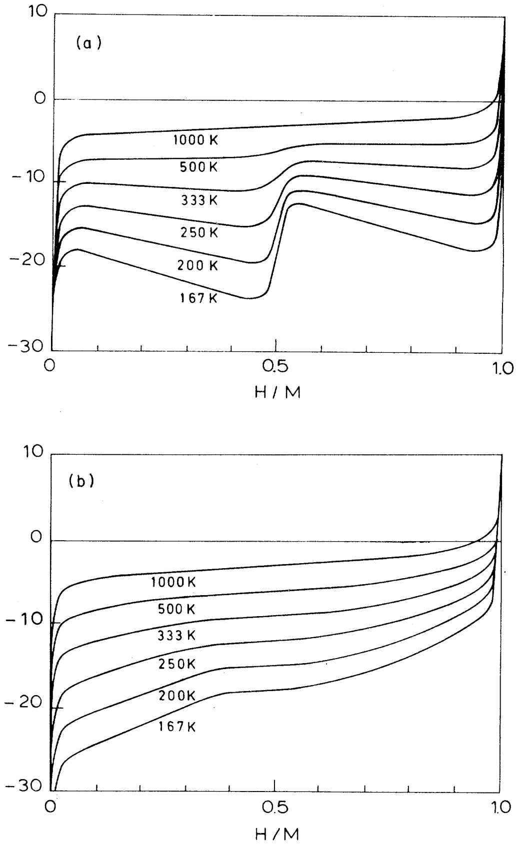

FIG. 5. Pressure-composition isotherms for hydrogen absorption in (a) a perfectly crystallized substance ($\Delta=0$) and (b) in an amorphous substance with $\Delta=0.172$ eV (2000 K). For both substances the hydrogen-hydrogen interaction is attractive [$a=-0.345$ eV (-4000 K)], $S=0.129$ eV (1500 K), and $E_0-E_b=-0.086$ eV (1000 K).

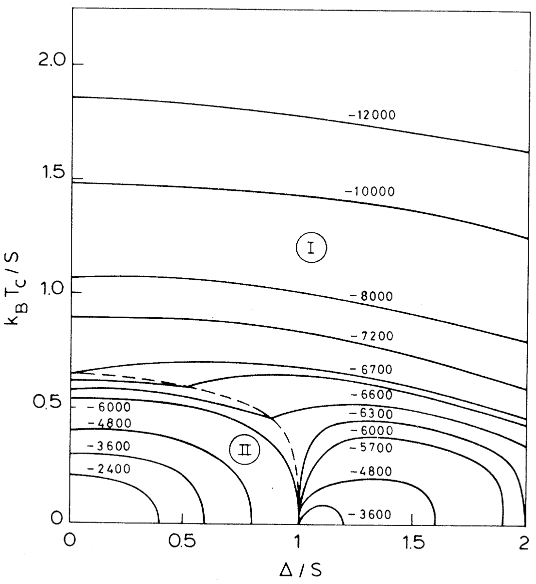

FIG. 6. Influence of disorder on the critical temperature of a metal hydrogen system with a double-square density-of-sites function [with $S=0.129$ eV ($=1500$ K) and $E_0-E_b=-0.086$ eV (-1000 K)] for various values of the hydrogen-hydrogen interaction parameters a (given in K).

$\Delta>S$, $T_c=0$ for $a=-2\Delta$. For $\Delta=S$ the double-square density-of-sites model reduces to the single-square model described above.

To conclude this section we show that the $Ni_{50}Zr_{50}H_x$ data in Fig. 1 can be reproduced qualitatively by means of the aforementioned simple models. In both crystalline and amorphous $Ni_{50}Zr_{50}$ we assume that the hydrogen-hydrogen interaction is attractive with $a=-0.4309$ eV (-5000 K). The plateau pressures can then be fitted with $E_0-E_b=-0.1896$ eV (-2200 K) and $S=0.181$ eV ($=2100$ K) (see Figs. 7(a) and 7(b)]. For the amorphous alloy the best fit is obtained by taking $S=\Delta=0.2585$ eV ($=3000$ K). The equality of S and Δ implies that in $Ni_{50}Zr_{50}$ the actual density-of-sites function may be simulated by a single-square distribution function of width $4S=1.034$ eV ($=12\,000$ K). It would be interesting to obtain a confirmation of this large value from an independent experiment such as internal friction or Gorsky effect.

IV. CONCLUSIONS

By means of a mean-field description of the hydrogen-hydrogen interaction we have shown that the critical temperature for hydrogen dissolved in a metal is positive if $-an(\mu_F^c)\geq 1$. This Stoner-type condition is not satisfied in systems which have (i) a low density of electronic states at E_F [see Eq. (8)] and/or (ii) a significant configurational disorder.

In Ni-Zr alloys the electron density of states $N(E_F)$ is relatively high[18,19] and the absence of phase separation is mainly due to disorder. For Pd-Si or Pd-Cu-Si (Ref. 20) alloys, on the other hand, the small value of $N(E_F)$ results in a positive (i.e., repulsive) hydrogen-hydrogen interaction (although the observed *expansion* of these alloys during hydrogenation implies that the elastic hydrogen-hydrogen interaction parameter a_{elast} is *negative)*. The absence of dissociation plateaus in these alloys is therefore

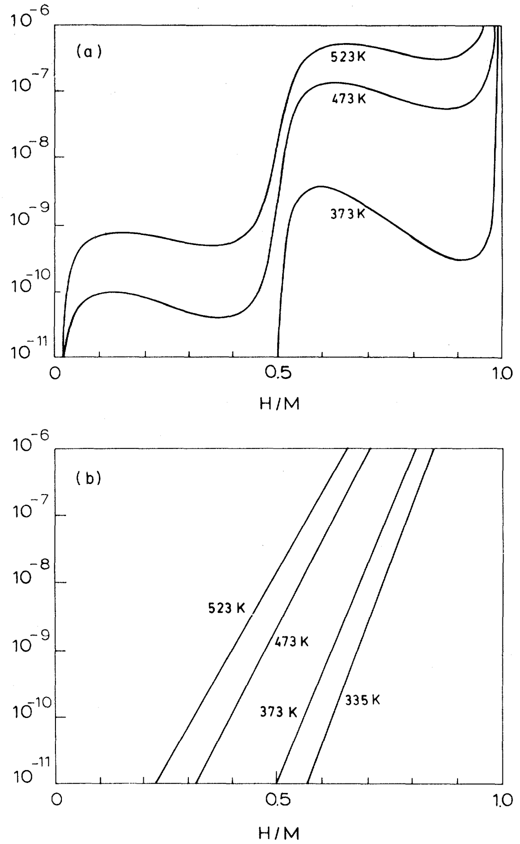

FIG. 7. Pressure-composition isotherms (without Maxwell construction) of (a) crystalline and (b) amorphous $Ni_{50}Zr_{50}$ as predicted by the double-square density-of-sites model. The values of the parameters E_0, S, and Δ used in the calculation of these isotherms are indicated in the text.

not primarily due to disorder. This explains why only minor changes occur in the hydrogen absorption isotherms of amorphous $Pd_{80}Si_{20}H_x$ (Ref. 5) and $Pd_{77.5}Cu_6Si_{16.5}H_x$ (Ref. 5) after recrystallization.

To conclude, it is interesting to make a prediction for which the amorphous metal-hydrides phase separation is most likely to occur. Since the strength of the elastic hydrogen-hydrogen interaction does not show strong variations from metal to metal, the parameter a will be most negative for alloys with a high density of electronic states at E_F, i.e., with a large electronic specific heat. Furthermore, the *crystalline* alloys should not have a large number of inequivalent interstitial sites, since in the amorphous state the broadening of the individual density-of-sites functions would result in a very broad total density-of-sites function and thus to a low value of $n(\mu_F^c)$. The latter requirement seems to favor binary alloys over ternary or quaternary metallic glasses. On the basis of these general arguments one would expect $Zr_{70}Pd_{30}$, $Zr_{70}Cu_{30}$, $La_{76}Au_{24}$, and $Zr_{76}Rh_{24}$ to be potential candidates for amorphous alloys with a positive critical temperature.

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