

Interstitial-site occupancies by H: A statistical model of blocking effects and H transition probabilities in fcc binary alloys

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Interstitial solid solutions of H in random fcc metal alloys have been examined in detail as far as the nature of interstitial sites and their spatial correlations are concerned. Both octahedral and tetrahedral sites have been considered and distinguished on the basis of the atomic composition and atomic arrangements within their first shell of neighbors. The conditional probability $q_{uu'}$ of finding a site of type u' as nearest neighbor of a given site of type u were calculated. Expressions for selective blocking factors and occupancy probabilities have been derived for the approximation of the hard-core model, assuming blocking of sites at distances smaller than about 0.21 nm from the occupied site. The application of the model to the $\text{Pd}_{1-y}\text{Pt}_y$ system shows that H solubility data can be interpreted on the basis of a site-filling process. Finally, transition probability factors have been estimated to predict the occurrence of anelastic relaxations.

I. INTRODUCTION

The location of H and D in pure crystalline metals, as well as in intermetallic compounds and metallic glasses has been extensively investigated over the past few decades.¹⁻¹² As a result of these investigations it is now well established that in fcc metals H and D occupy octahedral (O) interstitial sites (S),² while in bcc (Ref. 3) and hcp metals,⁴ as well as in $\text{Cu}_{50}\text{Ti}_{50}$ (Refs. 8 and 9) and $\text{Cu}_{50}\text{Zr}_{50}$ (Ref. 10) metallic glasses, occupancy of tetrahedral (T) sites is preferred. Deuterium in V appears to occupy both (O and T) types of sites.^{1,12}

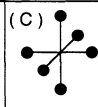
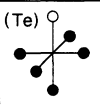
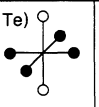
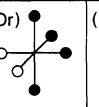
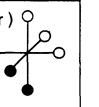
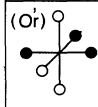
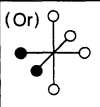
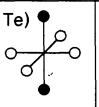
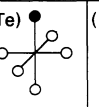
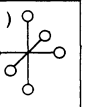
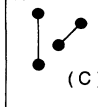
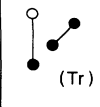
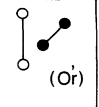
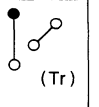
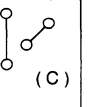
Several interstitial (I) sites can be energetically distinguishable in a binary alloy $A_{1-y}B_y$, depending on the chemical composition of the nearest and more distant shells of neighbors, as well as on the atomic arrangements within these shells.¹³ It therefore seems relevant to examine which type of sites may be occupied by H (and D) in binary alloys, particularly since occupancy of both T and O sites has recently been reported for $\text{Nb}_{1-y}\text{V}_y\text{H}_n$ alloys,¹⁴ which is contrary to what happens for the pure constituent metals.

In the last few years¹⁵ we have calculated the probabilities for octahedral site (OS) occupancies and for $\text{O} \leftrightarrow \text{O}$ transitions in random fcc alloys following concepts first applied to bcc lattices by Brouwer and Griessen¹⁶ and using some results by Hohler and Kronmüller.¹³ In view of the complexity of the problem, attention was confined to the OS, which were only distinguished one from another on the basis of the atomic composition of their first coordination shell of neighbors. In these investigations the probability of finding an OS in a selected position, next to a given type of site, has been calculated together with the jump probability factors for the interstitial H.

The main aim of the present work is to extend such calculations¹⁵ to include tetrahedral site occupancies, blocking effects and atomic arrangements within the first coor-

dination shell of neighbors. Blocking in these systems could arise from the occupation of T sites because the H-H distance between adjacent T and O sites will be less than 0.21 nm which is the commonly accepted minimum H-H separation. T occupation and the accompanying blocking will only be of importance in the relatively high pressure ranges where less favorable sites become occupied in Pd alloys. In addition, the work is aimed at the derivation of explicit expressions for the probabilities of

TABLE I. Octahedral ($u=1,2,\dots,10$) and tetrahedral ($u=11,12,\dots,15$) site configurations and their symmetries (C=cubic, Te=tetragonal, Tr=trigonal, Or= $\langle 110 \rangle$ orthorhombic, Or'= $\langle 100 \rangle$ orthorhombic). The included formulas give the site fractions p_u as a function of the alloy composition y ($z=1-y$).

$\sigma \backslash u$	1	2	3	4	5	
O						
	$1/3 \cdot z^6$	$2z^5y$	z^4y^2	$4z^4y^2$	$8/3 \cdot z^3y^3$	
	6	7	8	9	10	
						
	$4z^3y^3$	$4z^2y^4$	z^2y^4	$2zy^5$	$1/3 \cdot y^6$	
	T					
		$2/3 \cdot z^4$	$8/3 \cdot z^3y$	$4z^2y^2$	$8/3 \cdot zy^3$	$2/3 \cdot y^4$

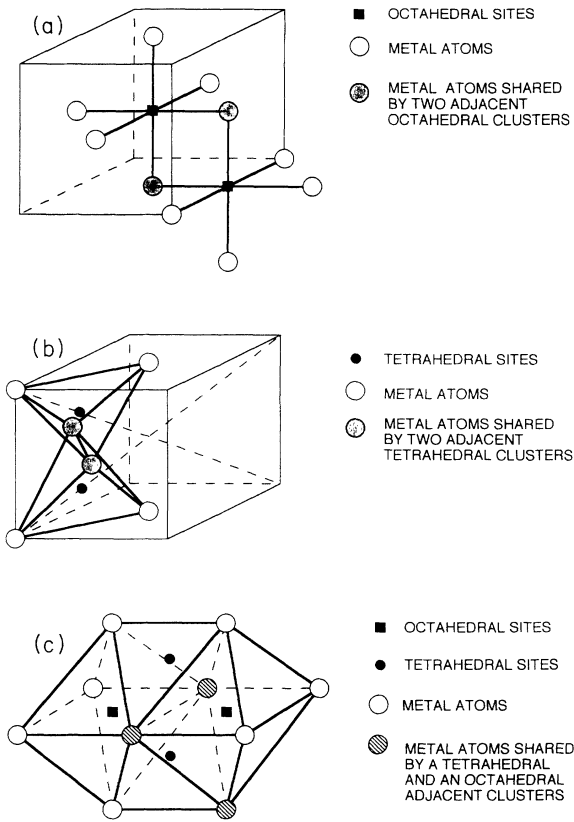


FIG. 1. Adjacent octahedral (a) and tetrahedral (b) atomic clusters surrounding interstitial sites in an fcc lattice. Two and three metal atoms are shared by adjacent clusters of the same and different types (a)–(c), respectively.

reorientational transitions of the H elastic dipole, which is a problem of major interest in anelastic studies of metal-hydrogen systems.

II. NATURE OF INTERSTITIAL SITES

In an fcc binary alloy fifteen types of interstitial sites can be distinguished, as shown in Table I, where the O and T sites are labeled with values from 1 to 10 and from 11 to 15, respectively, of an index, u . Their symmetry features, which are also indicated in Table I, can be cubic (C), tetragonal (Te), trigonal (Tr), $\langle 110 \rangle$ orthorhombic (Or) and $\langle 100 \rangle$ orthorhombic (Or'). The shells of neighbors have edges of length $a/\sqrt{2}$ (a =lattice parameter) and can be considered as filling the entire volume of the alloy. Each shell shares edges with adjacent shells of the same type and shares faces with adjacent shells of the other type [Figs. 1(a)–1(c)]. The structure is such that an OS has 8 nearest neighbors (nn) TS ($d_{O-T} = \sqrt{3}a/4$) and 12 next to nearest neighbors (nnn) OS ($d_{O-O} = a/\sqrt{2}$); a TS on the other hand, has 4 nn OS and 6 nnn TS ($d_{T-T} = a/2$).

In a random alloy the fractions p_u of the number of sites of type u and the total number M of sites, have been calculated by assuming a binomial distribution and by taking into account both the relative proportions of O and T sites (one to two) as well as the multiplicity of each configuration. The expressions for p_u as a function of y are recorded in Table I and plotted in Fig. 2.

III. SHORT-RANGE SPATIAL CORRELATIONS AMONG THE INTERSTITIAL SITES

In order to calculate the probability factors for H transitions from one site to another, spatial short-distance correlations among different types of sites need to be known as a function of the alloy composition y . For this purpose the conditional probabilities $q_{uu'}$ that, given a site of type u , another site selected among the nn of the first one is of type u' , have been calculated. The fact has been taken into account that adjacent atomic clusters of the same and different types share two and three atoms, respectively [Figs. 1(a)–1(c)].

The procedure followed is represented by the example given in Tables II(a) and II(b), referring to the case of two adjacent OS. Table II(a) shows the three allowed configurations for the two shared atoms as well as their occurrence conditional probabilities $P(j|u)$ ($j=1,2,3$). In Table II (b) the allowed configurations of the four nonshared atoms of the second generic shell of neighbors are displayed for each pair, together with their occurrence conditional probabilities $P(u'|j)$. The expressions of $q_{uu'}$ [$q_{uu'} = \sum_{j=1}^3 P(j|u)P(u'|j)$] were finally derived and are given in Tables III(a)–III(d), which refer to O-O ($u, u'=1,2, \dots, 10$), T-O ($u=11,12, \dots, 15$; $u'=1,2, \dots, 10$), O-T ($u=1,2, \dots, 10$; $u'=11,12, \dots, 15$) and T-T ($u, u'=11,12, \dots, 15$) combinations, respectively. Empty spaces in the tables correspond to probabilities equal to zero.

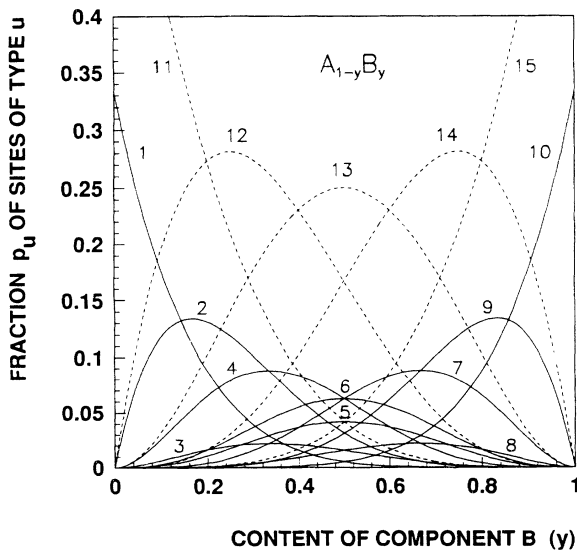


FIG. 2. Fractions p_u of octahedral ($u=1,2, \dots, 10$) and tetrahedral ($u=11,12, \dots, 15$) sites as distinguished by the different chemical composition and atomic arrangement within their first shell of neighbors.

IV. SITE ENERGIES

Following a procedure developed by Brouwer and Griessen¹⁶ for TS in bcc alloys, the first shell of neighbors has been considered to correspond to a cluster of composition $A_i B_{N-i}$ ($N=6$ for OS, $N=4$ for TS; $i=0, 1, \dots, N$) embedded in a matrix of average compo-

TABLE II. (a) Nature of the atom pair shared by an OS of given type u with an adjacent OS of any type and associated occurrence probabilities. (b) Configurations of nonshared atoms associated with each pair of (a) and their occurrence probabilities versus the average alloy composition y ($z=1-y$).

shared pair u	J		
	J=1	J=2	J=3
1	1	0	0
2	2/3	1/3	0
3	1/3	2/3	0
4	5/12	1/2	1/12
5	1/6	1/2	1/4
6	1/4	2/3	1/6
7	1/12	1/2	5/12
8	0	2/3	1/3
9	0	1/3	2/3
10	0	0	1

shared pair	configurations of the 4 non shared atoms				
J=1	1 Z^4	2 $4Z^3Y$	3 Z^2Y^2	5 $2ZY^3$	7 Y^4
			4 $5Z^2Y^2$	6 $2ZY^3$	
J=2	2 Z^4	3 Z^3Y	5 $2Z^2Y^2$	7 $3ZY^3$	9 Y^4
		4 $3Z^3Y$	6 $4Z^2Y^2$	8 ZY^3	
J=3	4 Z^4	5 $2Z^3Y$	7 $5Z^2Y^2$	9 $4ZY^3$	10 Y^4
		6 $2Z^3Y$	8 Z^2Y^2		

sition $A_{1-y}B_y$, and the site energies e_u have then been calculated by means of the relations

$$e_u = e_u^* - \frac{BV_H}{V_m}(\Omega_u - \Omega_u^*), \tag{1}$$

where V_m is the molar volume of the alloy, B is the bulk modulus, V_H is the volume change induced by a mole of H in solution in the alloy, e_u^* and Ω_u^* are the energy and volume of the free cluster (that is of a cluster embedded in an alloy with the same average composition as the cluster itself) and e_u and Ω_u are the energy and volume of the embedded cluster. Values for e_u^* and Ω_u^* could then be deduced from relation (13) of Ref. 16, when the electronic band structure parameters and the cluster volumes of the pure metals A and B are known. The parameter Ω_u has been taken as intermediate between Ω_u^* and the average cluster volume in the alloy $\bar{\Omega}$ according to the relation

$$\Omega_u = (1-d)\bar{\Omega} + d\Omega_u^* . \tag{2}$$

The parameter $d \in [0, 1]$ represents the force constant between nn atoms. In the course of the present work d has been calculated for TS (see the Appendix) in an fcc alloy following a procedure initially applied to TS in bcc alloys¹⁶ and to OS in fcc alloys.¹⁵ Results of the calculations are

$$\begin{aligned} d &= 0.812I' \quad (u = 1, 2, \dots, 10) , \\ d &= 0.750I' \quad (u = 11, 12, \dots, 15) . \end{aligned} \tag{3}$$

The quantity I' , which measures the average deviation of the mean lattice spacings in an alloy, can be estimated from Fig. 1 of Ref. 17, when elastic constant data of a particular alloy are available.

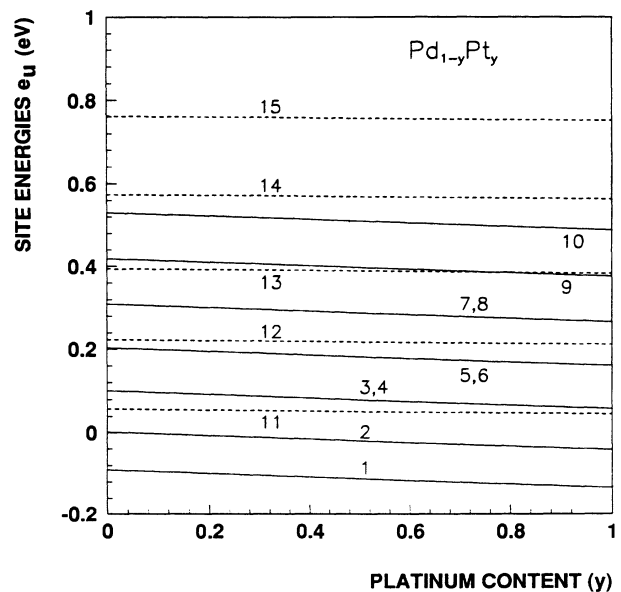


FIG. 3. Dependence on the platinum content of site energies e_u as deduced from the embedded cluster model [relation (1) in the text] for octahedral ($u=1, 2, \dots, 10$) and tetrahedral ($u=11, 12, \dots, 15$) sites.

TABLE III. (a) Probability $q_{uu'}$ of finding an OS of type u' in a selected interstitial position nn of an OS of type $u(u, u' = 1, 2, \dots, 10)$ in an $A_{1-y}B_y$ fcc alloy ($[i] = (1-y)y^{4-i}$, $i = 0, 1, \dots, 4$). (b) Probability $q_{uu'}$ of finding an OS of type u' in a selected interstitial position nn of a TS of type $u(u = 1, 12, \dots, 15; u' = 1, 2, \dots, 10)$ in an $A_{1-y}B_y$ fcc alloy ($z = 1 - y$). (c) Probability $q_{uu'}$ of finding a TS of type u' in a selected interstitial position nn of an OS of type $u(u = 1, 2, \dots, 10; u' = 11, 12, \dots, 15)$ in an $A_{1-y}B_y$ fcc alloy ($z = 1 - y$). (d) Probability $q_{uu'}$ of finding a TS of type u' in a selected interstitial position nn of a TS of type $u(u, u' = 11, 12, \dots, 15)$ in an $A_{1-y}B_y$ fcc alloy ($z = 1 - y$).

$u \backslash u'$	1	2	3	4	5	6	7	8	9	10
1	1[4]	4[3]	1[2]	5[2]	2[1]	2[1]	1[0]	$\frac{1}{3}[1]$	$\frac{1}{3}[0]$	$\frac{1}{2}[0]$
2	$\frac{2}{3}[4]$	$\frac{1}{3}[4] + \frac{8}{3}[3]$	$\frac{1}{3}[3] + \frac{2}{3}[2]$	$1[3] + \frac{4}{3}[1]$	$\frac{2}{3}[2] + \frac{4}{3}[1]$	$\frac{4}{3}[2] + \frac{4}{3}[1]$	$1[1] + \frac{2}{3}[0]$	$\frac{1}{3}[1]$	$\frac{1}{3}[0]$	$\frac{1}{2}[0]$
3	$\frac{1}{3}[4]$	$\frac{2}{3}[4] + \frac{4}{3}[3]$	$\frac{2}{3}[3] + \frac{1}{3}[2]$	$2[3] + \frac{5}{3}[2]$	$\frac{4}{3}[2] + \frac{2}{3}[1]$	$\frac{8}{3}[2] + \frac{2}{3}[1]$	$2[1] + \frac{1}{3}[0]$	$\frac{2}{3}[1]$	$\frac{2}{3}[0]$	$\frac{1}{2}[0]$
4	$\frac{5}{12}[4]$	$\frac{1}{3}[4] + \frac{5}{3}[3]$	$\frac{1}{3}[3] + \frac{5}{12}[2]$	$\frac{1}{12}[4] + \frac{3}{3}[3] + \frac{25}{12}[2]$	$\frac{1}{6}[3] + 1[2] + \frac{5}{6}[1]$	$\frac{1}{6}[3] + 2[2] + \frac{5}{6}[1]$	$\frac{5}{12}[2] + \frac{3}{2}[1] + \frac{5}{12}[0]$	$\frac{1}{12}[2] + \frac{1}{2}[1]$	$\frac{1}{3}[1] + \frac{1}{2}[0]$	$\frac{1}{12}[0]$
5	$\frac{1}{4}[4]$	$\frac{1}{4}[4] + 1[3]$	$\frac{1}{4}[3] + \frac{1}{4}[2]$	$\frac{1}{4}[4] + \frac{3}{4}[3] + \frac{5}{4}[2]$	$\frac{1}{2}[3] + 1[2] + \frac{1}{2}[1]$	$\frac{1}{2}[3] + 2[2] + \frac{1}{2}[1]$	$\frac{5}{4}[2] + \frac{3}{2}[1] + \frac{1}{4}[0]$	$\frac{1}{4}[2] + \frac{1}{2}[1]$	$1[1] + \frac{1}{2}[0]$	$\frac{1}{4}[0]$
6	$\frac{1}{6}[4]$	$\frac{2}{6}[4] + \frac{2}{3}[3]$	$\frac{2}{6}[3] + \frac{1}{6}[2]$	$\frac{1}{6}[4] + 2[3] + \frac{5}{6}[2]$	$\frac{1}{3}[3] + \frac{4}{3}[2] + \frac{1}{3}[1]$	$\frac{1}{3}[3] + \frac{8}{3}[2] + \frac{1}{3}[1]$	$\frac{5}{6}[2] + 2[1] + \frac{1}{6}[0]$	$\frac{1}{6}[2] + \frac{2}{3}[1]$	$\frac{2}{3}[1] + \frac{2}{3}[0]$	$\frac{1}{6}[0]$
7	$\frac{1}{12}[4]$	$\frac{1}{12}[4] + \frac{1}{3}[3]$	$\frac{1}{12}[3] + \frac{1}{12}[2]$	$\frac{5}{12}[4] + \frac{3}{3}[3] + \frac{5}{12}[2]$	$\frac{5}{6}[3] + 1[2] + \frac{1}{6}[1]$	$\frac{5}{6}[3] + 2[2] + \frac{1}{6}[1]$	$\frac{25}{12}[2] + \frac{3}{2}[1] + \frac{1}{12}[0]$	$\frac{5}{12}[2] + \frac{1}{2}[1]$	$\frac{5}{12}[1] + \frac{1}{2}[0]$	$\frac{5}{12}[0]$
8	$\frac{2}{3}[4]$	$\frac{2}{3}[4]$	$\frac{2}{3}[3]$	$\frac{1}{3}[4] + 2[3]$	$\frac{2}{3}[3] + \frac{4}{3}[2]$	$\frac{2}{3}[3] + \frac{8}{3}[2]$	$\frac{5}{3}[2] + 2[1]$	$\frac{1}{3}[2] + \frac{2}{3}[1]$	$\frac{4}{3}[1] + \frac{2}{3}[0]$	$\frac{1}{3}[0]$
9	$\frac{1}{3}[4]$	$\frac{1}{3}[4]$	$\frac{1}{3}[3]$	$\frac{2}{3}[4] + 1[3]$	$\frac{4}{3}[3] + \frac{2}{3}[2]$	$\frac{4}{3}[3] + \frac{4}{3}[2]$	$\frac{10}{3}[2] + 1[1]$	$\frac{2}{3}[2] + \frac{1}{3}[1]$	$\frac{8}{3}[1] + \frac{1}{3}[0]$	$\frac{2}{3}[0]$
10				1[4]	2[3]	2[3]	5[2]	1[2]	4[1]	1[0]

$u \backslash u'$	1	2	3	4	5	6	7	8	9	10
11	z^3	$3zy^2$	$3z^2y$	$3zy^2$	y^3	$\frac{3}{2}zy^2$	$\frac{3}{4}y^3$	$\frac{1}{2}zy^2$	$\frac{1}{2}y^3$	$\frac{1}{4}y^3$
12	$\frac{1}{4}z^3$	$\frac{3}{4}z^2y + \frac{3}{4}zy^2$	$\frac{3}{4}z^2y$	$\frac{3}{2}z^2y + \frac{3}{4}zy^2$	$\frac{3}{4}zy^2 + \frac{1}{4}y^3$	$\frac{3}{2}zy^2$	$zy^2 + \frac{1}{2}y^3$	$\frac{3}{4}zy^2$	$\frac{3}{4}y^3$	$\frac{1}{4}y^3$
13		$\frac{1}{2}z^3 + z^2y$	$\frac{1}{2}z^2y$	$\frac{1}{2}z^3 + z^2y$	$\frac{1}{2}z^2y + \frac{1}{2}zy^2$	$z^2y + zy^2$	$\frac{3}{4}z^2y + \frac{3}{2}zy^2$	$\frac{3}{4}zy^2$	$\frac{3}{2}zy^2 + \frac{3}{4}y^3$	$\frac{1}{4}y^3$
14		$\frac{3}{4}z^3$		$\frac{3}{4}z^3$	$\frac{1}{4}z^3 + \frac{3}{4}z^2y$	$\frac{3}{2}z^2y$	$3z^2y$		$3zy^2$	y^3
15					z^3					

$u \backslash u'$	11	12	13	14	15	$u \backslash u'$	11	12	13	14	15
1	z	y	$\frac{1}{2}y$			11	z^2	$2zy$	y^2	$\frac{1}{2}y^2$	$\frac{1}{6}y^2$
2	$\frac{1}{2}z$	$\frac{1}{2}$	y			12	$\frac{1}{2}z^2$	$\frac{1}{2}z^2 + zy$	$zy + \frac{1}{2}y^2$	$\frac{1}{3}zy + \frac{2}{3}y^2$	$\frac{1}{6}y^2$
3	z	z	y			13	$\frac{1}{6}z^2$	$\frac{2}{3}z^2 + \frac{1}{3}zy$	$\frac{1}{6}z^2 + \frac{4}{3}zy + \frac{1}{6}y^2$	$zy + \frac{1}{2}y^2$	$\frac{1}{2}y^2$
4	$\frac{1}{4}z$	$\frac{1}{2}z + \frac{1}{4}y$	$\frac{1}{4}z + \frac{1}{2}y$	$\frac{1}{8}y$	$\frac{1}{8}y$	14	$\frac{1}{6}z^2$	$\frac{1}{2}z^2 + zy$	$\frac{1}{2}z^2 + zy$	$2zy$	y^2
5	$\frac{1}{8}z$	$\frac{3}{8}z + \frac{3}{8}y$	$\frac{3}{8}z + \frac{3}{8}y$	$\frac{1}{8}z + \frac{3}{8}y$	$\frac{1}{8}y$	15		$\frac{1}{2}z^2$	$\frac{1}{2}z^2$		
6	$\frac{1}{2}z$	$\frac{1}{2}z$	$\frac{1}{2}$	$\frac{1}{2}y$	$\frac{1}{2}y$						
7	$\frac{1}{4}z$	$\frac{1}{2}z + \frac{1}{4}y$	$\frac{1}{2}z + \frac{1}{4}y$	$\frac{1}{4}z + \frac{1}{2}y$	$\frac{1}{4}y$						
8	z	z	z	z	z						
9	$\frac{1}{2}z$	$\frac{1}{2}z$	$\frac{1}{2}z$	$\frac{1}{2}z$	$\frac{1}{2}y$						
10				z	y						

This procedure has been applied to the Pd_{1-y}Pt_y alloy system taking for B , V_m , V_H , and I' the values given in Ref. 15 and the values given in Ref. 18 and in Ref. 19 for the quantities related to the electronic band structures of Pd and Pt. The assumption has been made that isocompositional clusters have the same volumes ($\Omega_3 = \Omega_4, \Omega_5 = \Omega_6, \Omega_7 = \Omega_8$) and are consequently energetically degenerate. The calculated values of e_u are plotted versus alloy composition in Fig. 3.

It is interesting to note that the energy of a given site depends on the average composition of the embedding alloy matrix, and, more importantly, that some of the tetrahedral sites are energetically favorable for H occupancy with respect to several of the O sites. The tetrahedral site I_{11} in particular appears to be the third lowest energy site. Although neglected in the present model, differences in the number and arrangement of atoms of species A (or B) within the second and more distant shells of neighbors are expected to give rise to splittings into bands of the energy levels of Fig. 3.

V. SITE OCCUPANCIES

In order to deduce the fractions c_u of the occupied sites, that is to say the number of interstitial atoms occupying a given type of site I_u divided by the total number M of the interstitial sites, the Fermi-Dirac statistics are the most suitable as has been discussed by Kirchheim.²⁰ Expressions for c_u involving H-H interactions have been provided,¹⁶ which, in principle, may be applicable up to the highest contents of hydrogen. The effect of short-range H-H interactions (repulsive) are accounted for in the framework of the hard-core model by the introduction of blocking factors, while contributions of long-range interactions (repulsive or attractive) are accounted for by the addition of a H concentration dependent term $f(c)$ to the site energies as represented by the relations

$$c_u = \frac{p_u}{s_u + \exp\{[e_u + f(c) - \mu]/kT\}} \quad (u = 1, 2, \dots, 15), \quad (4)$$

where μ is the chemical potential of H, s_u is a selective blocking factor indicating the number of sites of type I_u made unoccupable by a H atom already sitting in a site of the same type, $f(c)$ is an effective long-range interaction term dependent on the concentration c of hydrogen (here c is taken to be the ratio of the total number of H atoms to the total number M of interstitial sites). According to relation (4) the levels $e_u + f(c)$ which are lower than μ , at 0 K have occupation probabilities equal to $1/s_u$. Thus the short-range H-H interactions modify the form of the occupancy probability factor of the Fermi-Dirac statistics, making the procedure not fully satisfactory from a formal point of view. Furthermore, explicit expressions of s_u as a function of c_u are not available as yet, thus, limiting the usefulness of relation (4). For these reasons a formulation of relation (4) is proposed, where blocking effects are more conveniently accounted for by replacing the fractions p_u with the fractions $p_u - p_u^b$ of unblocked sites and keeping unchanged the occupation probability factor of the Fermi-Dirac statistics. This is equivalent to

saying that an increase of c changes the density of states, shifting to inaccessibly high energies a progressively increasing number of levels (the blocked ones). In conclusion, the following expressions for c_u are proposed

$$c_u = \frac{p_u - p_u^b}{1 + \exp\{[e_u + f(c) - \mu]/kT\}} \quad (u = 1, 2, \dots, 15). \quad (5)$$

Estimates of p_u^b will be made under the assumptions that an H atom sitting in an OS would prevent occupancy by another H atom of its 8 nn TS and that an H atom located in a TS, besides its 4 nn OS, would also prevent occupancy of its 6 nnn TS. These assumptions would fulfill the widely accepted criterion of an H-H minimum approaching distance within a metal hydride of 0.21 nm.²¹

Approximate expressions for the fractions p_u^b of blocked sites are as follows:

$$p_u^b = Z_u^0 \sum_{u'=11}^{15} c_{u'} q_{u'u}, \quad u = 1, 2, \dots, 10, \quad (6)$$

$$p_u^b = Z_u^1 \sum_{u'=1}^{10} c_{u'} q_{u'u} + Z_u^2 \sum_{u'=11}^{15} c_{u'} q_{u'u}, \quad u = 11, 12, \dots, 15. \quad (7)$$

The product $c_{u'} q_{u'u}$ in relation (6) represents the probability that a given site is an occupied tetrahedral site of type u' and, jointly, that a selected adjacent O site is of type u . Thus, the sum represents the probability that any given site is an occupied TS of any type having an OS of type u in a particular nn interstitial position. The factors Z_u^0 account for the overall interstitial positions of type O nn of an occupied TS as well as for multiple blocking of the same OS. At infinite hydrogen dilution, Z_u^0 will coincide with the number of OS nn to a tetrahedral site, that is to say with number 4. At higher H contents, blocking of the same OS of type u by more than one occupied TS will occur, and consequently, Z_u^0 will decrease. By analogy, Z_u^1 and Z_u^2 in relation (7) account for the number of TS of type u blocked by occupied O and T sites, respectively. For the case of pure bcc metals and for TS occupancy by H, approximate analytical expressions for the fraction of occupable sites have been calculated by Boureau.²² Unfortunately these calculations do not apply to the more complicated situation of alloys, where a multiplicity of sites are involved. For these systems the following approximate formulas for the selective blocking factors are suggested:

$$Z_u^0 = \frac{4}{1 + 4 \sum_{u'=11}^{15} q_{uu'} c_{u'} / p_{u'}} \quad (u = 1, 2, \dots, 10),$$

$$Z_u^1 = \frac{8}{1 + 3 \sum_{u'=1}^{10} q_{uu'} c_{u'} / p_{u'}} \quad (u = 11, 12, \dots, 15), \quad (8)$$

$$Z_u^2 = \frac{6}{1 + 5 \sum_{u'=11}^{15} q_{uu'} c_{u'} / p_{u'}} \quad (u = 11, 12, \dots, 15),$$

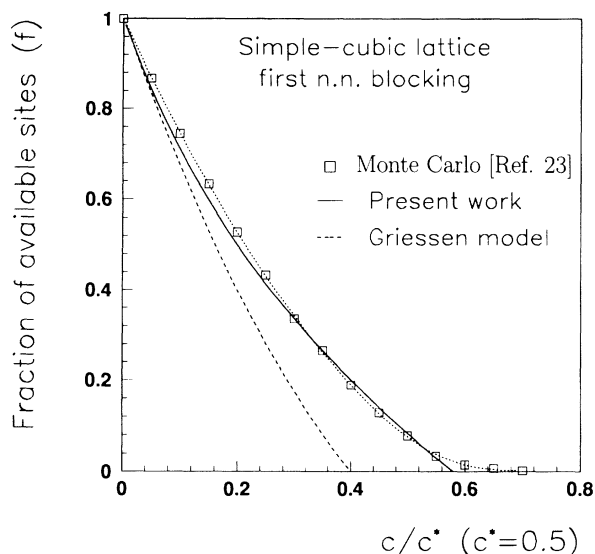


FIG. 4. Fraction of free sites, that is sites neither occupied nor blocked by interstitial atoms, in a simple cubic lattice.

where 4, 8, and 6 are the numbers of sites nn to the occupied one. The second term in the denominators expresses the average number of H atoms that, in addition to the given one, participate in the blocking process of the same site u ; the sum is the probability for occupancy by hydrogen of sites other than the occupied one which are nn to site u . The inverse of the denominator therefore gives the fractional contribution of a given H atom to the blocking process of one of its nn sites of type u . The contribution coming from sites nn to site u other than the given occupied one is, however, only estimated approximately, since their occupation probabilities have been assumed to be unaffected by site u being empty and the given one being filled. At the present time an exact evaluation of the required conditional probabilities is not possible. In the second term of the denominator of Z_u^0 the multiplying factor is 4 instead of 7 since three of the nn of site I_u are blocked by the occupied one.

For a test of the present model Monte Carlo computer simulations would be of paramount importance; these calculations, however, are difficult to make in the presence of a multiplicity of sites and blocking factors. Thus, a less stringent but still significant check has been carried out applying relations from (5) to (8) to a monoatomic simple cubic lattice, for which Monte Carlo simulations are available.²³

A comparison of the results obtained in the assumption that an interstitial atom blocks its six nn interstitial sites is presented in Fig. 4, where the fraction f of the free sites, that is of sites neither occupied nor blocked ($f = 1 - c - p^b$), is plotted against the concentration of interstitials normalized to the upper limit of the obtainable concentration c^* ($c^* = 0.5$). Brower and Griessen¹⁶ have not derived an expression for the concentration dependence of s_u and consequently of c_u . However, they suggested that a linear dependence of s on c between appropriate limits ($s = 6$ for $c \rightarrow 0$ and $s = 1$ for $c \rightarrow 0.5$ for

the simple cubic lattice) might have been a good approximation. This does not seem to be the case from the comparison in the same Fig. 4, where results derived from relation (4) under this assumption are also reported. On the other hand, the present model is in fairly good agreement with Monte Carlo simulations up to high concentrations c ($c < 0.55c^*$) of interstitial atoms.

Substitution of (6) and (7) into (5) leads to a nonlinear system of equations in the unknown quantities c_u . This system for dilute solid solutions of hydrogen can be approximated with a linear one, since the second term in the denominators of relations (8) are negligible with respect to unity and all the Z_u values can be identified with the number of sites nn to a site of type u .

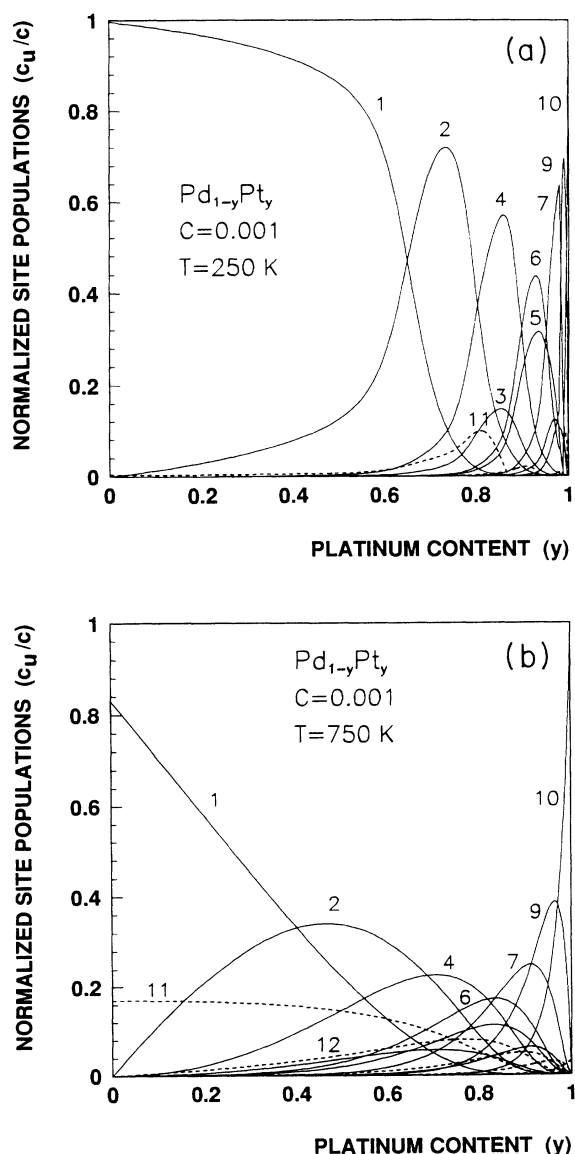


FIG. 5. Dependence on platinum content of the normalized site populations in dilute H solid solutions at two well separated temperatures for octahedral ($u = 1, 2, \dots, 10$) and tetrahedral ($u = 11, 12, \dots, 15$) sites.

In this approximation the normalized values of c_u have been calculated for $\text{Pd}_{1-y}\text{Pt}_y$ alloys by an iterative procedure in which the unknown quantity $f(c) - \mu$ has been used as a normalizing parameter in order to fulfill the condition $\sum_u c_u = c$. The results for a H content $c = 0.001$ and for the temperatures 250 and 750 K are plotted in Figs. 5(a) and 5(b) as a function of alloy composition. It can be seen that at 250 K all the levels except for I_1 and to a minor extent I_2 are virtually depopulated for platinum contents lower than about 0.5. However, at 750 K occupancies of higher energy sites, particularly of I_4 and I_{11} , have become appreciable at even low values of y and may, thus, substantially contribute to thermodynamical and diffusion properties of the H lattice gas.

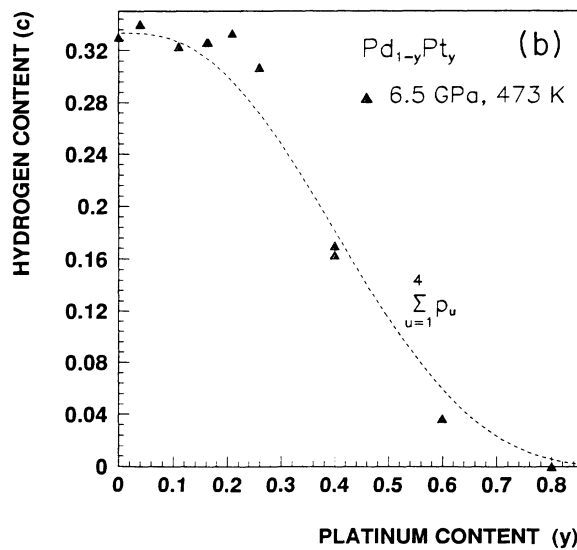
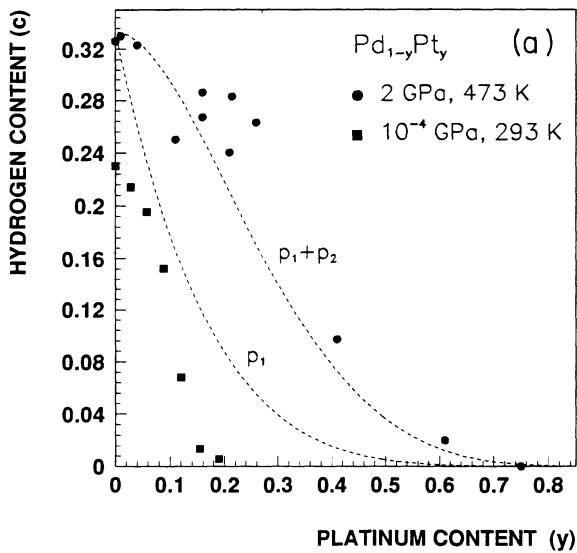


FIG. 6. H absorption by $\text{Pd}_{1-y}\text{Pt}_y$ alloys at constant pressure and temperature and some calculated cumulative fractions of the lowest energy sites vs platinum content; \cup from Ref. 23, Δ and \bullet from Ref. 26.

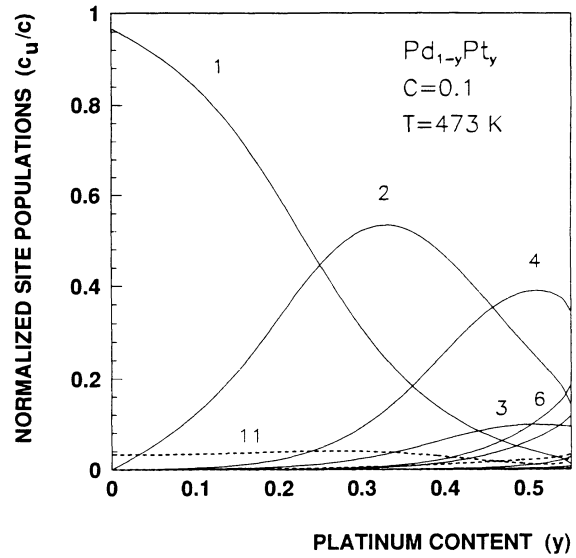


FIG. 7. Dependence on platinum content of the normalized H populations calculated from relation (5) in the text for octahedral ($u = 1, 2, \dots, 10$) and tetrahedral ($u = 11, 12, \dots, 15$) sites.

These considerations, however, should only apply to those alloys which are able to dissolve amounts of H up to $c = 0.001$.

In order to estimate the hydrogen capacity of $\text{Pd}_{1-y}\text{Pt}_y$ alloys isothermal or isobaric experiments such as those carried out in Refs. 24–27 are of particular relevance. The amounts of H absorbed as a function of y at 473 K for 2×10^9 and for 6.5×10^9 Pa of hydrogen pressure,²⁷ and at 293 K for 10^5 Pa (Ref. 24) are plotted in Figs. 6(a) and 6(b), where $p_1, p_1 + p_2$ and $\sum_{u=1}^4 p_u$ are also plotted for comparison. It is remarkable that the ex-

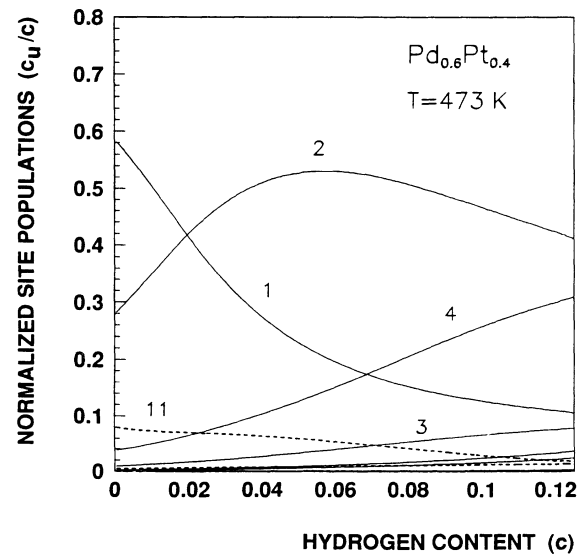


FIG. 8. Progressive filling by hydrogen of octahedral ($u = 1, 2, \dots, 10$) and tetrahedral ($u = 11, 12, \dots, 15$) sites for an alloy of a given platinum content ($y = 0.4$).

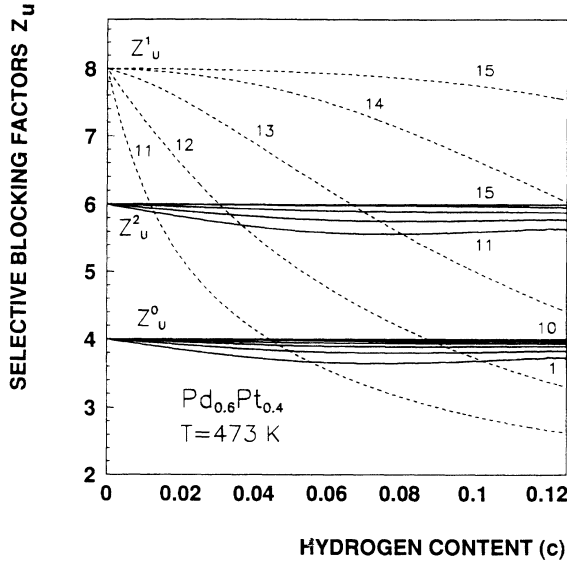


FIG. 9. Dependence on H concentration of the selective blocking factors Z_u^0 (blocking of octahedral sites by occupied tetrahedral sites), Z_u^1 (blocking of tetrahedral sites by occupied octahedral sites) and Z_u^2 (blocking of tetrahedral sites by occupied tetrahedral sites).

perimental data points at 10^5 , 2×10^9 and 6.5×10^9 Pa show similar dependences on the Pt content as those of $p_1, p_1 + p_2$ and $\sum_{u=1}^4 p_u$, respectively. This seems to demonstrate clearly that the limiting solubilities for a given pressure range are controlled by progressive filling of the lower energy sites.

For the high H content of $c = 0.1$ the normalized populations of sites by hydrogen were calculated by means of relations (5) for values of $y < 0.55$, as suggested by the data in Fig. 6(b). An iterative procedure was adopted, in which the quantities Z_u were used as parameters and automatically readjusted after each iteration in order to match the values of c_u calculated in the preceding cycle; this process was repeated until stable values of Z_u and c_u were obtained; the results are shown in Fig. 7. As suggested by Fig. 6(b), the results of the present analysis prove unambiguously that, at least at high hydrogen pressures, a wide spectrum of sites occupation occurs.

TABLE IV. (a) Probability \hat{q}_{uu} for an OS of type u of having a differently oriented identical site in a selected nn interstitial position ($u = 1, 2, \dots, 10$) in an $A_{1-y}B_y$ fcc alloy ($[i] = (1-y)^y y^{4-i}$, $i = 0, 1, \dots, 4$). (b) Probability \hat{q}_{uu} for a TS of type u of having a differently oriented identical site in a selected nn interstitial position ($u = 11, 12, \dots, 15$) in an $A_{1-y}B_y$ fcc alloy ($z = 1 - y$).

(a)										
u	1	2	3	4	5	6	7	8	9	10
\hat{q}_{uu}	$\frac{1}{3}[4] + \frac{5}{3}[3]$	$\frac{2}{3}[3]$	$\frac{4}{3}[3] + \frac{5}{3}[2]$	$\frac{1}{4}[3] + \frac{1}{2}[2] + \frac{1}{4}[1]$	$\frac{1}{6}[3] + \frac{5}{3}[2] + \frac{1}{6}[1]$	$\frac{5}{3}[2] + \frac{4}{3}[1]$	$\frac{2}{3}[1]$	$\frac{5}{3}[1] + \frac{1}{3}[0]$		
(b)										
u	11	12	13	14	15					
\hat{q}_{uu}		$\frac{1}{2}z^2 + \frac{1}{2}zy$	$\frac{2}{3}zy$	$\frac{1}{2}zy + \frac{1}{2}y^2$						

In Fig. 8 the progressive site filling process associated with increasing H contents is illustrated for the $Pd_{0.6}Pt_{0.4}$ alloy and the corresponding Z_u factors are plotted in Fig. 9. It can be observed that substantial changes with c are displayed by Z_u^1 , which may be associated with the high population of octahedral sites.

VI. TRANSITION PROBABILITIES

The probability for occurrence of an $I_u \rightarrow I_{u'}$ transition is proportional to c_u and to the fraction of sites $I_{u'}$ that can be occupied and which are nn of occupied sites I_u , that is to say, to the factor $\pi_{uu'}$ as given by

$$\pi_{uu'} = c_u q_{uu'} f_{uu'} \quad (9)$$

where $f_{uu'}$ represents the conditional probability that, given that I_u site is occupied, site $I_{u'}$ is neither occupied nor blocked by other H atoms. Some transitions are precluded due to geometrical restrictions, as is indicated by the zero values of some of the $q_{uu'}$ in Tables III(a)-III(d).

Within the approximation of the blocking model discussed in the previous section, the following expressions are obtained for $f_{uu'}$

$$f_{uu'} = 1 - \left[\frac{c_{u'}}{p_{u'}} + \frac{p_{u'}^b}{p_{u'}} \right] \quad (u, u' = 1, 2, \dots, 10) \quad (10a)$$

$$f_{uu'} = 1 - \frac{p_{u'}^b}{p_{u'}} \quad (u = 1, \dots, 10; u' = 1, \dots, 15) \quad (10b)$$

$$(u = 11, \dots, 15; u' = 1, \dots, 10) \quad (10b)$$

$$(u, u' = 11, \dots, 15) \quad (10b)$$

Due to blocking effects, the term $c_{u'}/p_{u'}$ vanishes for O-T, T-O, and T-T combinations of sites, as seen in relations (10b). Transitions associated with different values of u and u' lead to a change in the nature of the dipole resulting in a dipole-dipole reaction of the type

$$I_u \leftrightarrow I_{u'} \quad (u, u' = 1, 2, \dots, 15) \quad (11)$$

while those with identical values of u and u' may either cause a reorientation process, or leave the orientation of the H dipole unchanged, as happens for the example shown in Fig. 10 referring to transitions between pairs of

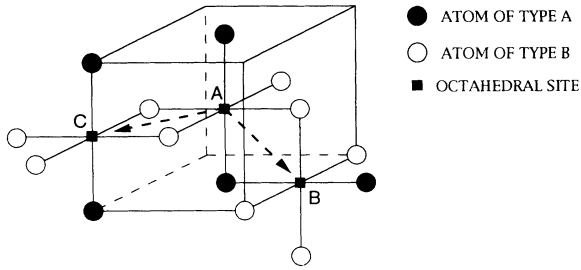


FIG. 10. Reorientational ($A \rightarrow B$) and nonreorientational ($A \rightarrow C$) transitions of the I_8 type of elastic dipole.

I_8 sites. The probability factors $\hat{\pi}_{uu}$ for reorientational transitions, which are consequently smaller than π_{uu} , are given by

$$\hat{\pi}_{uu} = c_u \hat{q}_{uu} f_{uu}, \quad (12)$$

where the probabilities \hat{q}_{uu} of one selected site nn to a given I_u site of being a differently oriented I_u site, are given in Tables IV(a) and IV(b).

VII. ANELASTIC RELATIONS

The formula deduced by Nowick and Heller²⁸ for the case of two dipole species of given molar concentrations has been generalized to N dipole species transforming one into the other in order to identify the stress-induced relaxations associated with H in an fcc alloy. For a homogeneous uniaxial stress σ_{11} , the result of the generalization is as follows:

$$\delta J = \frac{v_0}{kT} \sum_u \frac{C_u}{n_u} \left[\sum_s (\lambda_{11}^{us})^2 - \frac{1}{n_u} \left[\sum_s \lambda_{11}^{us} \right]^2 \right] + \frac{v_0}{9kT} \frac{1}{2} \sum_{u \neq u'} \frac{C_u C_{u'}}{C_t} (\text{tr} \lambda^u - \text{tr} \lambda^{u'})^2, \quad (13)$$

where δJ is the relaxation of the compliance J ; v_0 is the atomic (or molecular) volume; C_u and $C_{u'}$ are the mole fractions of species I_u and $I_{u'}$, respectively and C_t is equal to $\sum_u C_u$; λ_{11}^{us} is the component relative to orientation s of the dipole tensor λ^u .²⁸ The index s runs over the total number n_u of available orientations, which depends on the symmetry properties of the dipole. In the right-hand side of (13) the first summation corresponds to reorientational relaxations of anisotropic dipoles and the second corresponds to relaxations associated with reactions between different dipole species.

In the case of H in solution in an fcc alloy a situation occurs which is substantially different from those so far encountered in anelastic studies. In this case, due to blocking effects and to geometrical restrictions involved in the nature of I_u sites, only a fraction of the total amount of H will be involved in a specific relaxation process, this being the fraction of H atoms located in a certain type of sites and having an occupiable specific type of site as nn . This requires substitution in (13) of C_u with $3\hat{\pi}_{uu}$, $C_u C_{u'}$ with $9\pi_{uu'} \pi_{u'u}$ and of C_t with $3\sum_{u \neq u'} \pi_{uu'}$ (the numbers 3 and 9 occur because the probability fac-

tors are referred to the total number of sites M , while C_u and $C_{u'}$ are referred to that of metal atoms). Finally, relation (13) becomes

$$\delta J = \frac{3v_0}{kT} \sum_u \frac{\hat{\pi}_{uu}}{n_u} \left[\sum_s (\lambda_{11}^{us})^2 - \frac{1}{n_u} \left[\sum_s \lambda_{11}^{us} \right]^2 \right] + \frac{v_0}{3kT} \frac{1}{2} \sum_{u \neq u'} \pi_{uu'} \pi_{u'u} (\text{tr} \lambda^u - \text{tr} \lambda^{u'})^2 \quad (14)$$

where n_u is equal to 4,3,6,6 for Te,Tr,Or,Or' dipoles, respectively. Taking into account the selection rules indicated by the zeros of Tables III(a)–III(d), and the anisotropy of defects in Tables IV(a) and IV(b), 154 reaction terms and 11 reorientation terms can be, in principle, expected for relaxations in an fcc alloy containing hydrogen. As a consequence of the large number of contributions it may not be possible to resolve one relaxation from another and in some extreme cases they may only contribute to an increase of background dissipation. Of course relative magnitude of the various terms may differ considerably and most of them may be undetectable. For the case of $\text{Pd}_{1-y}\text{Pt}_y$ alloys, only jumps involving sites I_1, I_2 and to a minor extent I_4 and I_{11} can be expected to contribute and the strength of their associated relaxations will strongly depend on the alloy composition, total amount of hydrogen absorbed, and the temperature range of the investigations.

VIII. CONCLUSIONS

As discussed in the previous sections "H mechanical spectroscopy" in alloys is a puzzling problem and to be fully understood further progress will certainly be required. However, the calculation of the complete set of $q_{uu'}$ and \hat{q}_{uu} performed in the course of the present work, together with development of a procedure for estimating the populations c_u of the different sites, as well as of the selective blocking factors Z_u^0 (blocking of OS by occupied TS), Z_u^1 (blocking of TS by occupied OS) and Z_u^2 (blocking of TS by occupied TS) appears to be a step forward to a better understanding of metal-hydrogen systems. The application of the present model to the high and low pressure data concerning $\text{Pd}_{1-y}\text{Pt}_y$ alloys has clearly demonstrated that H limiting solubilities crucially depend on the availability of low energy sites in alloys with different Pt contents.

ACKNOWLEDGMENTS

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APPENDIX

Relation (A3) of Ref. 15 expressing d as a function of I' for octahedral clusters can be generalized to take into account both octahedral and tetrahedral clusters $A_i B_{N-i}$:

$$d \left[\frac{N-i}{N} - y \right] = \frac{3I'}{8N_B} \left[\frac{N_{B1}}{N_B} + \frac{N_{B2}}{N_B} \frac{d_2}{d_1} \right] \times [k_1(-2y) + k_2(2-2y) + k_3(1-2y)]. \quad (\text{A1})$$

Here N is the number of atoms in the cluster ($N=6$ for O clusters and $N=4$ for T clusters) and $N_B = \binom{N}{2}$ is the overall number of pairwise bonds, $N_{B1}(N_{B2})$ is the number of bonds between nearest neighbors (next nearest neighbors) and d_1 (d_2) their average separation distance; k_1, k_2 , and k_3 are the numbers of bonds of type AA , BB , and AB , respectively, and are given by

$$k_1 = \frac{i(i-1)}{2}, \quad k_2 = \frac{(N-i)(N-i-1)}{2}, \quad k_3 = i(N-i). \quad (\text{A2})$$

Combining relations (A1) and (A2) it follows that

$$d = \frac{3}{4} \left[\frac{N_{B1}}{N_B} + \frac{N_{B2}}{N_B} \frac{d_2}{d_1} \right] I'. \quad (\text{A3})$$

For T clusters $N_B = N_{B1} = 6$ and for O clusters $N_{B1} = 12$, $N_{B2} = 3$, and $d_2/d_1 = \sqrt{2}$. The following expressions are thus obtained for d

$$d = 0.75I' \quad (\text{TS}), \quad (\text{A4})$$

$$d = 0.812I' \quad (\text{OS}). \quad (\text{A5})$$

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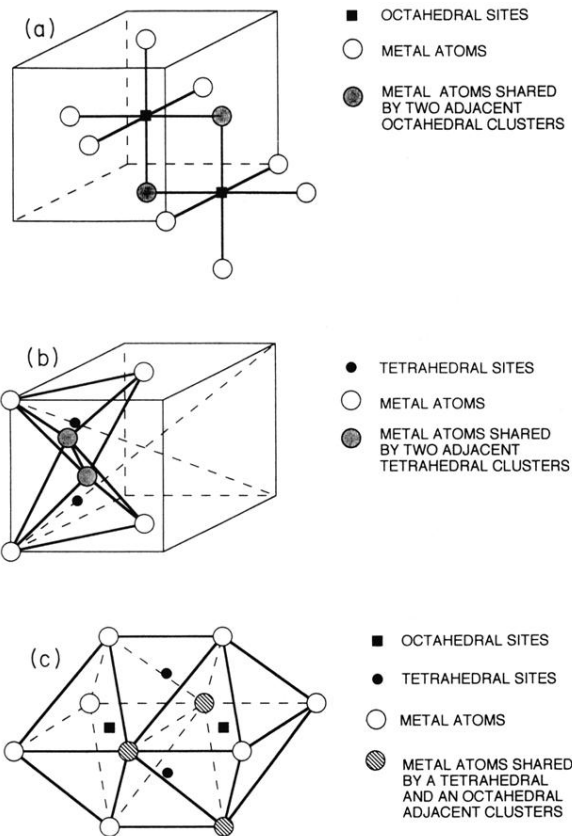


FIG. 1. Adjacent octahedral (a) and tetrahedral (b) atomic clusters surrounding interstitial sites in an fcc lattice. Two and three metal atoms are shared by adjacent clusters of the same and different types (a)–(c), respectively.