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Preferred hydrogen sites and hydride stoichiometry for A_6B_{23} compounds

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The variety of interstices available for potential occupation by hydrogen in A_6B_{23} intermetallic compounds makes them important tests of a geometric model recently developed for rationalizing observed hydride stoichiometries and preferred hydrogen sites. The model was applied to $Y_6Mn_{23}D_{18}$ and $Th_6Mn_{23}D_{16}$, for which structure determinations can be found in the literature. Both compounds have cubic structures of space group $Fm3m$, and they have 116 metal atoms per unit cell. Nine different kinds of sites (708 sites per unit cell) have been considered for potential occupancy. Hole radii and inter-site distances were calculated for all these types. Concepts of minimum hole radius (0.040 nm) and minimum H–H distance (0.210 nm) were used to predict hydrogen-site occupancy. The model correctly predicts that, in addition to a and f_3 sites, j_1 sites (Wyckoff notation) should be involved in both of these compounds at these H(D) concentrations. The location actually observed for the deuterium atom is in the hexahedral i site that has its centre in the trigonal face shared by two j_1 sites. For $Y_6Mn_{23}D_{23}$, the model correctly predicts the partial occupation of h sites, which are coordinated by two yttrium and three manganese atoms. Other predictions have been made, including one regarding partial occupation of l sites when there are more than 25 hydrogens per formula unit. The latter predictions have not been tested experimentally. With this crystal structure, both compounds appear to have a maximum absorption capacity of 33 hydrogens per formula unit.

1. Introduction

Recently, the structures of $Y_6Mn_{23}D_n$ ($n = 8.3$, 18 and 23) and $Th_6Mn_{23}D_{16}$ have been determined by neutron diffraction [1, 2]. The cubic structure of each belongs to space group $Fm3m$, and each has numerous types of interstices available for potential occupancy by H(D). This variety of sites makes the structure an important one for testing a geometric model recently developed [3] for rationalizing observed hydride stoichiometries and site occupancies. The important principles of the model are:

1. The volumes of metals and intermetallic compounds increase by roughly $0.0029\,nm^3$ per hydrogen atom added.
2. An interstice is not occupied by hydrogen in a stable hydride unless it is large enough to accommodate a sphere of radius 0.040 nm.
3. Other things being equal, larger holes tend to fill with H(D) first. It has been postulated [4] that, if metal A forms a more stable hydride than metal B, then H(D) may prefer those sites that are coordinated by the larger number of A atoms. In tests [3] of the model on AB_2 and AB_5 compounds, however, it was not necessary to invoke that criterion, because the radii of tetrahedral interstices decreased in the same order as the number of coordinating A atoms: A_2B_2, AB_3, B_4.
4. In a stable hydride, there is a minimum H–H distance of 0.210 nm.

The fundamental building block of Th_6Mn_{23} (or Y_6Mn_{23}) is shown schematically in Fig. 1; it is 1/32 of a unit cell. There are four octahedral a sites (A_6) per unit cell, 32 f_3 sites (A_3B), 96 k_1 sites (A_2B_2), 96 j_1 sites (AB_3), 96 j_2 sites (AB_3) and 192 l sites (AB_3). We have calculated that tetrahedral sites coordinated by four B atoms have radii, r_h, smaller than 0.040 nm, so we shall

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SYMBOL	ATOM OR INTERSTICE	WYCKOFF NOTATION
◯	A	24 e
▨	B	4 b
⬤	B	24 d
▩	B	$32\ f_1$
▧	B	$32\ f_2$
□	I	4 a
▲	I	$32\ f_3$
★	I	48 i
○	I	$96\ j_1$
•	I	$96\ j_2$
△	I	$96\ k_1$
◇	I	192 ℓ

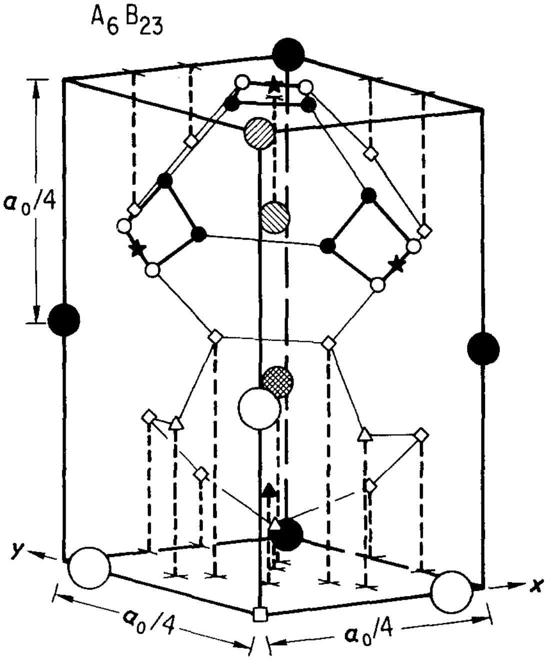

Figure 1 Model of the basic building block for A_6B_{23} intermetallic compounds (space group *F*m3m). Volume shown is 1/32 of a unit cell.

give them no further consideration. There are 48 i sites that are located at the centres of the trigonal faces shared by pairs of j_1 sites. Such a site may be thought of as coordinated by three equidistant B atoms and two equidistant A atoms; as such, it is a hexahedral interstice. The value of r_h is determined by the size and position of the B atoms. There are also 48 h sites located at the centres of the trigonal faces shared by two k sites. These hexahedral h sites are, also, coordinated by two A atoms and three B atoms. In addition there are 96 k_2 sites located at the centres of the trigonal faces shared by two l sites, and they are coordinated by one A atom and four B atoms.

In a comparison of the results [1, 2] for $Y_6Mn_{23}D_{18}$ and $Th_6Mn_{23}D_{16}$ some discrepancies were reported [5] but, as we shall discuss later, some of these may not be real. The present work is an application of a simple geometric model to a rather complex structure in an attempt to rationalize observed [1, 2] hydrogen-site preferences.

2. Application of the model

2.1. $Y_6Mn_{23}D_n$

2.1.1. $n = 18$

The compound $Y_6Mn_{23}D_{18}$ has $a_0 = 1.2799$ nm and the position parameters of the metal atoms have been reported [1]. The metal-atom radii r_Y and r_{Mn} are given [6] as 0.1773 nm and 0.1307 nm, respectively. From this information, we have calculated the radii of the largest spheres that could be accommodated by the various interstices and the position parameters for the centres of these spheres. The results are shown in Table I. In Table II, we show our calculated distances between the centres of spheres in neighbouring interstices.

We begin by letting deuterium occupy all of the a sites. These are by far the largest holes, they are coordinated by the largest number of yttrium atoms and they are very widely separated (> 0.9 nm). The second largest holes are the f_3, and these are coordinated by three yttrium atoms. The a–f_3 distance is only slightly less than 0.210 nm, so a deuterium atom in an f_3 site need be located only slightly off centre of the large f_3 hole to avoid violating the minimum distance criterion. All f_3 sites can be filled.

The sites designated k_1 are next largest and are coordinated by two thorium atoms, but none can be filled because the f_3–k_1 distance is far less than 0.210 nm. The j_1 and j_2 sites are nearly the same size and both are coordinated by one thorium atom. We note, however, that j_2 sites form an irregular hexagonal ring (Fig. 1), such that only

TABLE I Coordination, hole radii and position parameters for interstices in $Y_6Mn_{23}D_{18}$. Space group $Fm3m$

Site (Wyckoff)		Coordination		r_h (nm)	x	y	z
Number	Type	Yttrium	Manganese				
4	a	6	0	0.1196	0	0	0
32	f_3	3	1	0.0681	0.0943	0.0943	0.0943
96	k_1	2	2	0.0522	0.1547	0.1547	0.0473
96	j_1	1	3	0.0412	0	0.1409	0.3284
96	j_2	1	3	0.0426	0	0.0744	0.3869
48	i	2	3	0.0390	0.5000	0.1563	0.1563
192	l	1	3	0.0372	0.0796	0.1458	0.2537
48	h	2	3	0.0435	0	0.1538	0.1538
96	k_2	1	4	0.0270	0.1119	0.1119	0.2530

one site in the ring can be occupied at any given time. Furthermore, the shortest j_2–j_2 distance for sites in two different "building blocks" (Fig. 1) is only 0.1904 nm, and the result is that only sixteen j_2 sites could be filled simultaneously in a unit cell. Jacob [5] has erroneously referred to these sites as l_2.

A j_1 site has only one other j_1 site as a very near neighbour (0.0555 nm), and, as a result, 48 j_1 sites could be filled simultaneously, if there were no occupancy of j_2 sites. If sixteen j_2 sites were occupied, only 32 j_1 sites could be occupied at the same time. In either case the total number of deuterium atoms in j_1 and j_2 sites would be 48.

Both the i sites and the l sites have $r_h <$ 0.040 nm, although the i site is only slightly smaller than the criterion value: $r_h = 0.0390$ nm. For the moment, let us say that no i sites and no l sites are filled. At this point, let us take inventory. We have four deuterium atoms in a sites, 32 deuterium atoms in f_3 sites and 48 deuterium atoms in j_1 and j_2 sites, for a total of 84 deuterium atoms per unit cell, or 21 deuterium atoms per formula unit of Y_6Mn_{23}. Thus, there are more than enough available sites to account for deuterium absorption to a composition of $Y_6Mn_{23}D_{18}$. One might speculate that, at lower temperatures, almost all j_2 sites would be emptied by ordering, while increasing the temperature of $Y_6Mn_{23}D_{18}$ would cause increased occupation of j_2 sites up to a maximum of four deuterium atoms per formula unit.

TABLE II Distances between neighbouring interstices in $Y_6Mn_{23}D_{18}$

Site	Inter-site distance (nm)							
	a	f_3	k_1	j_1	j_2	l	i	h
a	0.9050	0.2091	0.2864	0.4574	0.5042	0.3882	0.4833	0.2769
f_3	0.2091	0.5635	0.1247	0.3285	0.3942	0.2152	0.3504	0.1608
k_1	0.2864	0.1247	0.1211 0.1944	0.2311	0.3202	0.1338 0.2030 0.2064	0.2495	0.0606
j_1	0.4574	0.3285	0.2311	0.0555 0.2551	0.1134 0.1294 0.2172	0.1399 0.1798 0.2239	0.0277	0.2250
j_2	0.5042	0.3942	0.3202	0.1134 0.1294 0.2172	0.0702 0.1346 0.1802 0.1904 0.2048	0.2187 0.2529 0.2546	0.1184 0.2283	0.3158
l	0.3882	0.2152	0.1338 0.2030 0.2064	0.1399 0.1798 0.2239	0.2187 0.2529 0.2546	0.1198 0.1887 0.1952 0.2039	0.1616 0.2450	0.1646
i	0.4833	0.3504	0.2495	0.0277	0.1184 0.2283	0.1616 0.2450	0.2828	0.2442
h	0.2769	0.1608	0.0606	0.2250	0.3158	0.1646	0.2442	0.2800

For this composition range, let us make a comparison with experimental results. Commandre *et al.* [1] have shown that only a sites and f_3 sites are occupied in $Y_6Mn_{23}D_{8.3}$, and that, in addition, the j_1 sites play a role when n increases from 8.3 to 18. Actually the position parameters attributed to these additional deuterium atoms place them only about 0.02 nm from i sites, the trigonal saddle points between pairs of j_1 sites. According to Table I, the radius of this trigonal i site is only slightly smaller than r_h for a j_1 site. As mentioned earlier, the i site can be thought of as coordinated by three manganese atoms and two yttrium atoms, so it is actually hexahedral. Jacob [5] refers to the i site as a "distorted octahedral", but we believe there is no advantage to such a designation. It may be important to note that the geometric model predicts $Y_6Mn_{23}D_{21}$ for maximum filling of a, f_3 and i sites, which is exactly the composition obtained by Buschow [7] when he charged Y_6Mn_{23} under one atmosphere of hydrogen at room temperature.

2.1.2. 21 $< n <$ *25*

As the lattice absorbs hydrogen, hole sizes and inter-site distances increase. Thus, at higher concentrations of deuterium, r_h for l sites might be expected to exceed 0.040 nm and make them available for occupancy. On the other hand, there is another contingency that may explain values of $n > 21$.

For the case of $ZrNiD_m$, we have shown [8] that a tetrahedral interstice coordinated by four zirconium atoms is occupied in ZrNiD, but that this preferred site is emptied in favour of two smaller sites with fewer coordinating zirconium atoms in $ZrNiD_3$. This phenomenon is necessitated by the fact that m cannot exceed 1.0 so long as the preferred site is filled, even at elevated pressures, because of the H–H distance criterion. Thus, in the present study, sites occupied at low values of n are not necessarily occupied at higher values of n.

For $Y_6Mn_{23}D_n$, we postulate that values of $n > 21$ could be attained by the emptying of f_3 sites, which would allow some involvement of k_1 sites. As shown in Table I, there are 96 such sites per unit cell and they have Y_2Mn_2 coordination. Because nearest-neighbour and second neighbour k_1 sites are separated by only about 0.12 nm and 0.19 nm, respectively, only eight k_1 sites could be filled per formula unit and there would seem to be no increase in n caused by filling k_1 sites instead of f_3 sites. We note, however, that the h site, situated at the centre of the trigonal face shared by two k_1 sites, may provide an alternative. The h site is very large: in $Y_6Mn_{23}D_{23}$, $r_h = 0.0500$ nm; in $Y_6Mn_{23}D_{18}$, $r_h = 0.0435$ nm. It is coordinated by two yttrium atoms and three manganese atoms, the same as the i site, which is reported to be occupied [1]. The shortest h–h distance is 0.2795 nm, and the shortest h–i distance is greater than 0.24 nm, so all h sites could be occupied. There are twelve h sites per formula unit, representing an increase of four deuterium atoms per formula unit over full occupancy of f_3 sites. The total number of deuterium atoms, therefore, that could occupy sites of types a, h, and i is 25 per formula unit. The proximity of h and l sites makes significant filling of l sites unlikely in $Y_6Mn_{23}D_{25}$. In fact, all other sites coordinated by at least one yttrium atom would be blocked. This value of $n = 25$, is precisely that reported by Malik *et al.* [9], who prepared their sample by reaction at room temperature with 60 atm of hydrogen pressure.

The large size of the h site, even in $Y_6Mn_{23}D_{18}$, leads us to suspect that these sites could begin to fill, with concomitant emptying of f_3 sites, at $n < 21$. If so, there might not be a separate plateau in the pressure–composition–temperature diagram for the composition range $21 < n < 25$; instead, the plateau could begin at $n < 21$.

The foregoing analysis appears to be in full agreement with the experimental results of Commandre *et al.* [1]. They reported that it is the involvement of k_1 sites that allows the formation of $Y_6Mn_{23}D_{23}$. The h site involves two k_1 sites, and we calculate that the centre of the h site is only 0.013 nm from the centre of the deuterium atom they assign to a k_1 site.

2.1.3. $n >$ *25*

From the lattice parameter for $Y_6Mn_{23}D_{23}$ (1.284 nm) [1], we calculate $r_h = 0.0384$ nm for l sites. This is only slightly greater than the value in $Y_6Mn_{23}D_{18}$ (Table I). Thus, from hole-size considerations, also, we do not expect significant occupation of l sites for $n = 25$. It still seems possible, however, that very high hydrogen pressure could cause the formation of a higher hydride in which l sites could be involved.

A model of the lattice formed by l sites was constructed for visualization of the closest possible,

TABLE III Coordination, hole radii and position parameters for interstices in $Th_6Mn_{23}D_{16}$. Space group *F*m3m

Site (Wyckoff)		Coordination		r_h (nm)	x	y	z
Number	Type	Thorium	Manganese				
4	a	6	0	0.0967	0	0	0
32	f_3	3	1	0.0531	0.0969	0.0969	0.0969
96	k_1	2	2	0.0455	0.1591	0.1591	0.0456
96	j_1	1	3	0.0479	0	0.1352	0.3270
96	j_2	1	3	0.0548	0	0.0766	0.3786
48	i	2	3	0.0446	0.5000	0.1541	0.1541
192	l	1	3	0.0373	0.0764	0.1449	0.2512
48	h	2	3	0.0370	0	0.1582	0.1582
96	k_2	1	4	0.0262	0.1097	0.1097	0.2507

three-dimensional packing of deuterium atoms in these interstices. While the short l–l distances are almost unchanged when n increases from 18 to 23 (0.1185 nm, 0.1889 nm, 0.1968 nm and 0.2074 nm for comparison with Table II), the model allows one to ascertain that all blocked sites would be multiply blocked in such a way that exactly one half of the l sites (24 per formula unit) could be filled simultaneously. With 24 l sites occupied, however, all h and i sites would have to be empty. We note that the l–f_3 distance is greater than 0.210 nm, so it would be possible for eight f_3 sites to be occupied by deuterium. With one deuterium in the a site, the maximum value of n would seem to be 33.

We have considered, also, whether deuterium might be situated at k_2 sites, the centres of trigonal faces shared by pairs of l sites, which would be analogous to the occupation of h and i sites. We calculate, however, that the hole radius for k_2 increases only slightly (0.0270 to 0.0288 nm) as n increases from 18 to 23. We submit, therefore, that k_2 sites would probably be too small for occupation, even for $n = 33$. Presently, it is not known whether hydrogen pressures greater than the 60 atm used by Malik *et al.* [9] would allow the preparation of $Y_6Mn_{23}H_n$ with $n > 25$.

2.2. $Th_6Mn_{23}D_{16}$

The compound $Th_6Mn_{23}D_{16}$ has $a_0 = 1.2922$ nm and the position parameters of the metal atoms have been reported [2]. The metal-atom radii [6] of thorium and manganese are 0.1798 nm and 0.1307 nm, respectively. From this information we have calculated the radii of the various interstices (Table III) and the inter-site distances (Table IV).

There are only a few differences in application of the model to $Y_6Mn_{23}D_{18}$ and $Th_6Mn_{23}D_{16}$. In the thorium compound, the a–f_3 distance exceeds 0.210 nm and one does not need to invoke an off-centre position for deuterium atoms in f_3 sites. Also, in the thorium compound, the fifth neighbour j_2–j_2 distance exceeds 0.210 nm, so it is possible to place five deuterium atoms per formula unit in j_2 sites instead of four. Actually, neither of these differences changes the conclusion that j_1 sites must play an important role. On the basis of size, one might expect the i sites to be occupied in $Th_6Mn_{23}D_{16}$ because they are even larger in that compound than in $Y_6Mn_{23}D_{18}$. Indeed, Hardman *et al.* [2] reported finding deuterium at a site only 0.026 nm from what we calculate to be the centre of the i site. In addition, they found that all f_3 sites contained deuterium atoms, but that sites of type a were empty. This latter point is anomalous; the a site is very large, it is coordinated by six thorium atoms, and the f_3–a distance exceeds 0.210 nm.

Hardman *et al.* [2] reported a plateau in the pressure–composition–temperature diagram for Th_6Mn_{23}–D for $16 < n < 24$. This may be interpreted as follows: The solubility limit is reached when all of the f_3 sites and two-thirds of the i sites have been filled. An increase in pressure causes a phase transformation, i.e., a discontinuous change in both deuterium concentration and a_0. With r_h greater than 0.040 nm, h sites are filled in lieu of f_3 sites. Just as in $Y_6Mn_{23}D_n$, the plateau should end near $n = 25$, and at room temperature, it does [2]. Hardman *et al.* [2], however, studied deuterium-site occupation for $n = 16$, only.

Speculation in Section 2.1.3 regarding occupation of l sites and a maximum $n = 33$ is relevant for $Th_6Mn_{23}D_n$, also. After charging Th_6Mn_{23} with hydrogen at a pressure of 60 atm, Malik *et al.* [9] reported a composition of $Th_6Mn_{23}H_{30}$. We believe that the reported [9] difference in

TABLE IV Distances between neighbouring interstices in $Th_6Mn_{23}D_{16}$

Site	Inter-site distance (nm)							
	a	f_3	k_1	j_1	j_2	l	i	h
a	0.9137	0.2168	0.2967	0.4573	0.4986	0.3875	0.4893	0.2892
f_3	0.2168	0.5597	0.1317	0.3265	0.3861	0.2105	0.3531	0.1688
k_1	0.2967	0.1317	0.1177 0.2075	0.2270	0.3097	0.1269 0.1984 0.2050	0.2486	0.0615
j_1	0.4573	0.3265	0.2269	0.0690 0.2471	0.1031 0.1286 0.2102	0.1397 0.1831 0.2245	0.0345	0.2211
j_2	0.4986	0.3861	0.3097	0.1031 0.1286 0.2102	0.0819 0.1400 0.1943 0.1980 0.2219	0.2113 0.2482 0.2493	0.1087 0.2263	0.3147
l	0.3875	0.2105	0.1269 0.1984 0.2050	0.1397 0.1831 0.2245	0.2113 0.2482 0.2493	0.1251 0.1899 0.1921 0.1976	0.1577 0.2451	0.1614
i	0.4893	0.3531	0.2486	0.0345	0.1087 0.2263	0.1577 0.2451	0.2816	0.2426
h	0.2892	0.1688	0.0615	0.2211	0.3147	0.1614	0.2426	0.2908

hydrogen-absorption capacity for Th_6Mn_{23} and Y_6Mn_{23} may be attributable to differences in hydride stability. Under sufficient hydrogen pressure, both Y_6Mn_{23} and Th_6Mn_{23} may be able to absorb 33 hydrogen atoms.

3. Conclusion

The variety of interstices in the large unit cells of the intermetallic compounds Y_6Mn_{23} and Th_6Mn_{23} make them important test cases for a geometric model recently developed to rationalize the stoichiometries and preferential hydrogen sites in the hydrides of metals and intermetallic compounds. In the model, only those sites with hole radii greater than 0.040 nm are allowed to be filled with hydrogen, and two sites cannot be occupied simultaneously unless they are separated by more than 0.210 nm. Even with several types of sites occupied at a given hydrogen concentration, the model can rationalize the experimentally observed site occupancy, with one possibly important exception. That exception is the fact that the large, octahedral site of type a is reported [2] to be empty in $Th_6Mn_{23}D_{16}$. The predictions of the model suggest at least three experiments:

1. For $Th_6Mn_{23}H_n$, it is conceivable that concentrations of $10 \leqslant n \leqslant 14$ could be achieved with hydrogen occupying sites of types a, f_3 and j_2. Does this occur, or does hydrogen prefer the smaller i sites (coordinated by two thorium atoms) over the larger j_2 sites (coordinated by one thorium atom) even in this concentration range?

2. For $Th_6Mn_{23}H_{30}$, the model predicts occupation of a, f_3 and l sites. Are the predictions correct?

3. Can one prepare $Y_6Mn_{23}H_n$ with $n > 25$ by using hydrogen pressures greater than 60 atm? If so, are l sites occupied?

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