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Hydrogen Sites in A_2BH_y (A = Ca, Sr, Eu; B = Ir, Rh, Ru)*

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A geometric model has been applied to the A_2BH_y hydrides (deuterides), Eu_2IrD_5, Ca_2IrH_5, Sr_2IrD_5, Ca_2RhH_5, Sr_2RhH_5, Ca_2RuH_6, and Sr_2RuD_6, none of which can be synthesized directly by reaction of hydrogen (deuterium) gas with an A_2B compound. Hole radii and intersite distances were calculated for the two types of interstices in each compound. There are two very large cubical interstices per formula unit. These are coordinated by eight atoms of type A, but they must remain unoccupied in A_2BH_y with $y = 5$ (or 6), because of their proximity to the square pyramidal interstices, of which there are six per formula unit. The geometric model allows rationalization of the occupation of these pyramidal sites. Despite the very significant chemical differences between the compounds considered here and those for which the model was initially developed, the present results showed no inconsistency with geometric criteria requiring that occupied interstices in stable hydrides have minimum hole radii of 0.40 Å and minimum hydrogen–hydrogen distances of 2.10 Å. Published results indicate that the seemingly related compound Mg_2NiD_4 does not conform to these empirical rules, and this case is discussed.

Introduction

In one of his review papers, Gibb (*1*) has stated: "It is tempting to essay a purely geometric interpretation of hydride formation, viz. that metals with large atomic interstices can take up hydrogen more readily than those with small atoms and therefore small interstices." He warned, however, that "the satisfying of maximum bonding potential and electrostatic attraction would appear to be more basic and reliable guides to the formation and nature of such compounds than the relative atomic and interstitial sizes." Thus, while Hägg (*2*) reported an average effective radius of 0.46 Å for the hydrogen atom in hydrides of Ti, Zr, V, and Ta, Gibb (*1*) suggested that the use of such rules for interstitial compound formation not be encouraged, except as an approximate guide. Similarly, we (*3, 4*) have pointed out that the success of a geometric model (*5–13*) in rationalizing the observed stoichiometries and preferred hydrogen sites in the hydrides of intermetallic compounds demands "an explanation based on the underlying fundamental principles." Nevertheless, the fact remains that a model based on only two geometric criteria (minimum hole size of 0.40 Å and minimum H–H distance of 2.10 Å) has been found to be applicable to the stable hydrides of intermetallic compounds containing a wide variety of metallic constituents and existing in numerous crystallograhic structures (*5–13*).

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As the applicability of the geometric model is shown to be more and more nearly universal, there appears to be a greater and greater need for theoretical explanation.

Prior to the present work, the geometric model (*5–13*) had not been tested on intermetallic compounds containing atoms of metals that form ionic hydrides, such as the alkali metals or the alkaline earths (excluding Be, which forms a covalent hydride). Neither had the model been tested on any compound containing atoms of a 4*d*- or 5*d*-metal from Group VIII. All the compounds considered in the current investigation contain atoms from one or both of these classes of metals.

All of the compounds we have considered heretofore react exothermically and reversibly with hydrogen gas, but the compounds considered presently are unstable with respect to hydrogen removal. For example, the Friauf–Laves phase $ZrCr_2$ is typical of the compounds studied previously; it absorbs hydrogen from the gas phase to form $ZrCr_2H_3$ with lattice expansion but no shuffling of the metal atoms, and the reaction is reversible. On the other hand, Sr_2IrD_5 is more nearly typical of the compounds considered in the present paper, and it is prepared (*14*) according to the reaction

$$2SrH_2 + Ir + \frac{1}{2}H_2 \rightarrow Sr_2IrH_5.$$

Thus, formation of this hydride is not simply a process of hydrogen atoms jumping from interstice to interstice in an existing matrix until they find their preferred sites, as would be the case for the hydrogenation of $ZrCr_2$. Hence, the current investigation tests the validity of the models's geometric criteria for some hydrides that cannot be synthesized by direct reacion of an intermetallic compound with hydrogen gas.

For the hydrides studied earlier, when there were different types of interstices having radii greater than 0.40 Å, hydrogen atoms exhibited a preference for the larger interstices (*5–13*). Larger sites can be emptied, however in favor of more numerous, but smaller, sites if the formation of higher hydrides requires it (*8*). For the present study, this is apparently especially significant, because the structures of the compounds considered here include very large cubical interstices that are reported to be unoccupied.

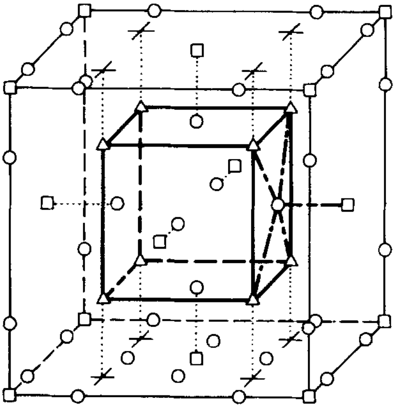

FIG. 1. Schematic diagram of a unit cell of A_2BH_y (cubic, space group *Fm*3*m*). △, *A* atoms; □, *B* atoms; ○, H sites. All H sites in the bottom face of the unit cell are shown, but four H sites have been deleted from each of the other faces for clarity. An example of each of the two types of interstices is shown: a cubical interstice is coordinated by all eight *A* atoms in the unit cell, and a square pyramidal interstice is coordinated by four *A* atoms and a *B* atom (right side of the diagram). When all of the pyramidal sites are occupied by H atoms, $y = 6$.

Moyer *et al.* (*14, 15*) determined the structures of Ca_2IrH_5, Sr_2IrH_5, Ca_2RhH_5, Sr_2IrD_5, Ca_2RuH_6, and Sr_2RuH_6 and found that the Group VIII metals form a face-centered cubic sublattice with alkaline earth metals at the centers of the tetrahedral interstices (Fig. 1). The space group is *Fm*3*m* with Group VIII metals in 4*a* sites, alkaline earth metals in 8*c* sites, and the hydrogen atoms in 24*e* sites (*x*00), with *x* slightly less than $\frac{1}{4}$. Thus, the hydrogen atom is located inside a square pyramidal interstice and

TABLE I

LATTICE PARAMETERS FOR THE VARIOUS COMPOUNDS

Compound	Eu_2IrD_5	Ca_2IrH_5	Sr_2IrH_5	Ca_2RhH_5	Sr_2RhH_5	Ca_2RuH_6	Sr_2RuH_6
a_0 (Å)	7.580	7.29	7.62	7.24	7.60	7.24	7.60
Ref.	(*17*)	(*14*)	(*14, 16*)	(*14*)	(*14*)	(*14*)	(*14*)

near its base. Four alkaline earth atoms constitute the base and the Group VIII metal is at the apex. At the center of the unit cell and at the center of each edge is the center of an octahedral interstice in the sublattice of Group VIII atoms. More importantly, however, these are the centers of the cubical interstices of the simple cubic sublattice of alkaline earth atoms. Each of these 4*b* sites is surrounded by six of the 24*e* square pyramidal interstices. Subsequent studies (*16, 17*) of Sr_2IrD_5 and Eu_2IrD_5 confirmed all these generalizations concerning structure.

Calculations

Just as in the earlier studies (*5–13*), the hole radius r_h was calculated with the assumption that the radii of the metal atoms are the metallic radii (for coordination number 12) as compiled by Teatum *et al.* (*18*). Thus, r_M = 1.357, 1.345, 1.339, 1.974, 2.151, and 1.798 Å for M = Ir, Rh, Ru, Ca, Sr, and Eu, respectively. The lattice parameters are given in Table I.

Results

There are two basic types of interstices in the cubic structures of those compounds listed in Table I. There are cubical interstices (c) at the body center and at the midpoints of the edges of each unit cell, and there are square pyramidal interstices (p), whose bases are the faces of those c sites. The hole radii for the interstices are shown in Table II, along with the reported (*14, 16, 17*) position parameters for the deute-

TABLE II

HOLE RADII FOR THE INTERSTICES OF THE VARIOUS COMPOUNDS AND POSITION PARAMETERS FOR THE 24*e* SQUARE PYRAMIDAL SITES

Compound	Eu_2IrD_5	Ca_2IrH_5	Sr_2IrH_5	Ca_2RhH_5	Sr_2RhH_5	Ca_2RuH_6	Sr_2RuH_6
r_h (Å) cubical	1.24	1.18	1.16	1.16	1.14	1.16	1.14
r_h (Å) pyramidal	0.64	0.61	0.55	0.59	0.54	0.59	0.54
x pyramidal (calculated)	0.264	0.270	0.250	0.267	0.248	0.266	0.247
x pyramidal (Ref.)	0.22 (*17*)	—	0.224 0.233 (*16, 14*)	—	—	—	0.223 (*14*)
x pyramidal (adjusted)	0.23	0.24	0.23	0.24	0.23	0.24	0.23

rium atoms and our calculated position parameters for the centers of the pyramidal interstices.

Obviously, the c sites are much larger than the p sites, but there are only four c sites per unit cell. Thus, if all c sites (but only c sites) were occupied, there would be only two hydrogen atoms per formula unit (Sr_2IrD_2, for example). The calculated separations of the c sites and the p sites for the various compounds range from 1.68 to 1.93 Å; in no case, therefore, could hydrogen atoms occupy the two types of sites simultaneously, according to the minimum H–H distance of 2.10 Å criterion. Apparently, in compounds A_2BD_y with $y = 5$ (or 6), only the p sites, of which there are six per formula unit, can be occupied.

We note several instances in Table II for which the calculated value of x for the 24e pyramidal sites is greater than 0.25. If the deuterium atom were situated with $x >$ 0.25, its center would lie just outside the base of the p site. We submit, therefore, that the deuterium nucleus might be found, instead, at $x < 0.25$, but at a distance from the Group VIII metal that still allows for a hydrogen atom radius = 0.4 Å. With this allowance, we calculate the values of x shown at the bottom of Table II. These adjusted values appear to agree well with the values of x determined by neutron diffraction (*14, 16, 17*), i.e., for Eu_2IrD_5, Sr_2IrD_5, and Sr_2RuD_6.

In all cases, the separation of p sites greatly exceeds 2.10 Å, so all of them can be occupied simultaneously. Adjusting the values of x downward from the initial results, where some values were greater than 0.25, increases the separation of the deuterium atom from the center of the c site. For all the compounds in Table II, however, that separation is still less than the criterion value of 2.10 Å, and the prediction of empty c sites is unchanged. In agreement with the available experimental results, the model predicts hydrogen occupation of the square pyramidal interstices to a maximum of six hydrogen atoms per formula unit.

Discussion

Like the deuterides considered in the present study, Mg_2NiD_4 (*19*) has constituent metal atoms from Group IIA and from Group VIII. It is different, however, in that it can be synthesized by direct reaction of Mg_2Ni and D_2. Structurally, it is very similar; it has a fcc sublattice of Ni atoms with Mg atoms in the tetrahedral interstices of that sublattice. From neutron diffraction results, Schefer *et al.* (*19*) found the lattice parameter $a_0 = 6.49$ Å, and they reported that deuterium atoms were randomly distributed in 24e sites for which $x = 0.226$. From our point of view, that value of x is a very surprising result for two reasons:

(1) It demands a D–Ni distance of only 1.467 Å. From (*18*) we obtain 1.246 Å for the metallic radius of a nickel atom. Obviously, the difference (0.221 Å) is only about half the criterion value of 0.40 Å for the radius of an occupied interstice in a stable hydride.

(2) With $x = 0.226$, the intersite distance for the six sites surrounding a given Ni atom would be only 2.074 Å, which is slightly less than the minimum of 2.10 Å required in the model. The pressure–composition–temperature plots and the structural results presented by Schefer *et al.* (*19*) leave no doubt that Mg_2NiH_4 is a hydride and not a solid solution of hydrogen. Thus, the geometric model would require $x \geq (1.247 + 0.40\ \text{Å})/a_0 = 0.254$, a condition that would place the deuterium atom just outside the base of the square pyramid and inside the cubical interstice. The separation of these nearest neighbor 24e sites with $x =$ 0.254 would be 2.258 Å, thereby exceeding the minimum H–H distance required in the geometric model. The intersite distance for the six sites surrounding a given Ni atom

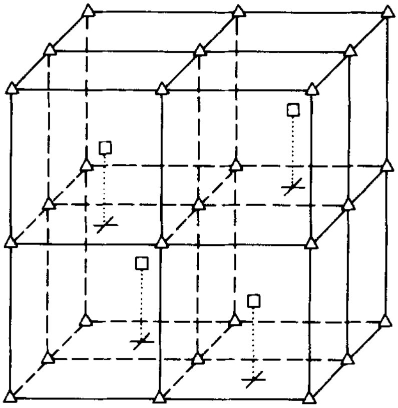

FIG. 2. Structure of $A_2B\text{H}_y$ with H sites deleted. The origin has been shifted by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ relative to Fig. 1. This diagram allows one to perceive the structure as a simple cubic array of A atoms with alternate cubes having their body centers occupied by B atoms.

would be 2.331 Å. From the model, therefore, one would predict that each cubical interstice coordinated by eight Mg atoms should have a random distribution of four deuterium atoms situated very near the centers of its six faces. In this configuration, the Mg–D distance (2.295 Å) is virtually the same as that reported (2.300 Å) by Schefer *et al.* (*19*).

The model disagrees with the experimental results only in the fact that it requires a D–Ni distance of 1.646 Å compared with the reported (*19*) value of 1.467 Å. Such a short D–Ni distance leads to violations of both geometric criteria in the model: minimum hole size and minimum H–H radius. In applications of the geometric model to hydrides of ZrNi (*7*, *8*), LaNi_5 and its alloys (*6*) and Ti_2Ni (*20*), the hole radii of occupied interstices were never smaller than 0.40 Å, which allowed D–Ni distances to be consistently greater than 1.646 Å. Because the reported (*19*) D–Ni distance for Mg_2NiD_4 fails to conform to the empirical rules that are found to be valid for numerous other seemingly related compounds, a reexamination of that experimental result may be warranted.

Shoemaker and Shoemaker (*21*) proposed that it may not be possible for tetrahedra sharing a common face to be occupied simultaneously by hydrogen atoms. Seemingly, an extension of that restriction would also require that no interstice could accommodate more than one hydrogen atom at a time. The prediction of the geometric model for Mg_2NiD_4 contradicts such a restriction, because it places four deuterium atoms within the boundaries of the cubical interstice. One may be able to justify such behavior by taking a different view of the crystallographic structure.

The structure shown in Fig. 1 may be perceived as a simple cubic sublattice of A atoms (Fig. 2). There are eight unit cells of this sublattice per unit cell of the compound. The B atoms are located in alternate unit cells of the A sublattice. Thus, if we consider Sr_2RuH_6, for example, a cell of the A sublattice that contains a Ru atom contains six hydrogen atoms, as well, because that cell is constituted by six occupied square pyramidal interstices. The prediction of the geometric model for Mg_2NiD_4 is that alternating unit cells of the A sublattice are of two types: one contains a body-centered B atom, while the other contains four (nearly) face-centered deuterium atoms. Hence, a comparison between the prediction of the model for Mg_2NiD_4 and the observations reported (*14–17*, *19*) for A_2BD_y compounds with this structure reveals that the only difference is the proposed very slight shift of the deuterium atoms in {100} directions, such that their centers are located inside the otherwise empty cubical interstices instead of inside those cubical interstices that contain the body-centered Ni atoms.

Conclusion

The compounds investigated here are unstable with respect to hydrogen removal. Nevertheless, their maximum hydrogen concentrations and preferred interstices can be rationalized by the same geometric model developed earlier for intermetallic compounds that are stable during absorption or desorption of hydrogen. Prior to this study, the model had not been tested on any compounds containing either elements that form ionic hydrides or the 4*d* and 5*d* elements of Group VIII. Apparently, the bonding of hydrogen to these constituent atoms obeys the same geometric rules as had been adopted earlier for intermetallic compounds containing a wide variety of other metals. A published value of the D–Ni distance in the cubic form of Mg_2NiD_4 does not conform to these rules.

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