

## Comparison of Bonding Characteristics of Hydrogen in $Ti_2Pd$ and $Pd_2Ti$ Alloys

Dae-Bok Kang

Department of Chemistry, Kyungsoong University, Busan 608-736, Korea. E-mail: dbkang@ks.ac.kr  
Received February 28, 2011, Accepted April 15, 2011

The electronic structure and bonding in  $Ti_2Pd$  and  $Pd_2Ti$  alloys with and without hydrogen as an interstitial atom were studied by performing extended Hückel tight-binding band calculations. The hydrogen absorption near an octahedral site is found to be a favorable process in  $Ti_2Pd$  rather than in  $Pd_2Ti$ . In metal hydrides, the metal-hydrogen bonding contribution is crucial to the stability of the system. The stronger interaction of hydrogen with Ti atoms in  $Ti_2PdH_2$  than with Pd atoms in  $Pd_2TiH_2$  is analyzed by perturbation theory.

**Key Words** : Hydrogen storage materials, Electronic structure, Extended Hückel calculations

### Introduction

There is a substantial technological interest in the inter-metallic compounds as materials for hydrogen storage, particularly for a viable hydrogen fuel in vehicular applications.<sup>1-4</sup> Compared with other technologies such as gas compression or liquefaction, solid-state materials such as metal alloys can store hydrogen at relatively low pressure and ambient temperatures.

The traditional interstitial metal hydrides have been successfully utilized.<sup>5</sup> Over the past few decades, a major challenge which still remains is to identify optimal inter-metallic for such purposes. The hydrogen sorption properties of these alloys are very much dependent on the constituents and metal-hydrogen bonding interactions play a major role for the stability of the hydrides. A better understanding of the role of individual alloy constituents in relation to the presence of hydrogen and the subsequent influence on electronic and structural properties may eventually lead to more efficient devices with higher storage capacities.

Several members of the  $A_2B$  intermetallic compound family with the tetragonal  $MoSi_2$ -type crystal structure can absorb hydrogen to produce ternary metal hydride phases.<sup>6</sup> We use the Ti-Pd intermetallic compounds,  $Ti_2Pd$  and  $Pd_2Ti$ , as model systems.  $Ti_2Pd$  is known for its hydrogen storage capability,<sup>7</sup> whereas for  $Pd_2Ti$ , this property still needs to be proven.<sup>8,9</sup> The compound  $Ti_2Pd$  readily forms a hydride to give a nominal composition  $Ti_2PdH_2$ . Surprisingly,  $Pd_2Ti$  does not form a hydride under normal condition although both Ti and Pd are good hydride forming metals. It is of interest to try to understand the reasons for the hydrogen inertness of this compound.

In the present work we examine the origin of this puzzling behavior. It will be useful to eliminate the possibility of geometrical considerations first, since hydrogen occupation is not restricted by geometrical criteria for the minimum hole size and intersite distance in the lattice of  $Pd_2Ti$ . Thus, the different hydriding behaviors of the two intermetallics,  $Ti_2Pd$  and  $Pd_2Ti$ , can be understood in terms of their electronic structures and bonding characteristics. Since  $Pd_2TiH_2$  does

not exist, its crystal structure is assumed to reveal the factors that disfavor hydride formation in this compound. These computational results may be helpful for designing new  $A_2B$ -type hydrogen storage alloys with high efficiency.

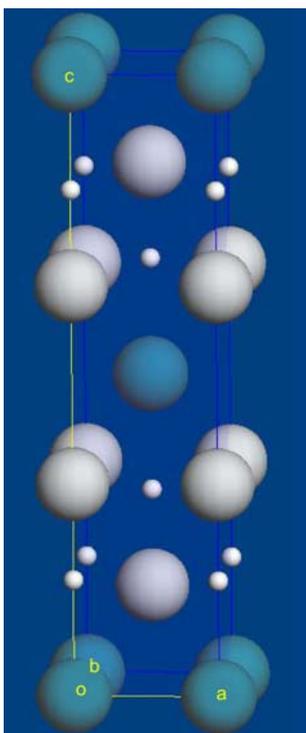
We use the extended Hückel tight-binding (EHTB) method<sup>10,11</sup> to determine the influence of hydrogenation on the electronic structures of the  $Ti_2Pd$  and  $Pd_2Ti$  alloys and to discuss the electronic consequences of the relevant orbital interactions of incorporating H with the intermetallics. Double zeta expansions of the metal d orbitals were employed; the parameters used for all atoms are listed in Table 1. Although the EH method is quite approximate, the analysis of orbital interactions by perturbation theory seems to be reasonably reliable. The CAESAR package<sup>12</sup> was used to calculate the density of states (DOS) and the crystal orbital overlap population (COOP) spectra of pure and hydrogenated  $Ti_2Pd$  and  $Pd_2Ti$  structures. While the DOS provides information about the band structure and the distribution of various orbitals in energy, the COOP curves describe the nature of the bonds between constituent atoms, with positive and negative values indicating bonding and antibonding states, respectively. Looking at the COOP, we may analyze the extent to which specific states contribute to a bond between atoms.

### Crystal Structure

Both  $Pd_2Ti$  and  $Ti_2Pd$  crystallize in the  $MoSi_2$ -type

**Table 1.** Parameters used for EHTB calculations

Atom	Orbital	$H_{ii}$ (eV)	$\zeta_1$	$\zeta_2$	$c_1$	$c_2$
Ti	4s	-6.3	1.5			
	4p	-3.2	1.5			
	3d	-5.9	4.55	1.40	0.4206	0.7839
Pd	5s	-7.32	2.190			
	5p	-3.75	2.152			
	4d	-12.02	5.983	2.613	0.5535	0.6701
H	1s	-13.6	1.3			



**Figure 1.** The tetragonal unit cell of  $\text{Ti}_2\text{PdH}_2$ . Large white, large blue, and small white spheres are for Ti, Pd, and H, respectively.

structure (space group  $I4/mmm$ ). The latter compound has a body-centered tetragonal structure with lattice constants  $a = 3.09 \text{ \AA}$  and  $c = 10.054 \text{ \AA}$ .<sup>13</sup> There are two formula units of  $\text{Ti}_2\text{Pd}$  per unit cell with a single  $2a$  Pd site  $(0,0,0; 0.5, 0.5,0.5)$  and a single  $4e$  Ti site  $(0,0,z; 0,0,1-z; 0.5,0.5,0.5+z; 0.5,0.5,0.5-z)$ . The Ti ( $4e$ ) and Pd ( $2a$ ) sites have an axial symmetry around  $c$ -axis (see Figure 1).

The hydrogen atom occupies an octahedral interstitial site formed by four titanium atoms in its base bicapped with Ti and Pd atoms, which provides an optimum environment satisfying the geometrical criteria for hydride formation. Such criteria have been established empirically.<sup>14,15</sup> They imply minimal values for the H-H distances and the interstitial hole radii of about 2.1 and 0.4  $\text{\AA}$ , respectively, for stable hydrides. Examination of the unit cell shows, as indicated in Figure 1, that there are four octahedral sites per unit cell surrounded completely by metal atoms. These are found to be the preferred sites for hydrogen occupation.<sup>16</sup> A complete filling of those sites in the lattice corresponds to a composition of  $\text{Ti}_2\text{PdH}_2$ . For the purpose of comparison with the case of  $\text{Ti}_2\text{PdH}_2$ , we assume that the hydride form of hypothetical  $\text{Pd}_2\text{TiH}_2$  can be stabilized in  $\text{MoSi}_2$ -type structure.  $\text{Ti}_2\text{Pd}$  and  $\text{Pd}_2\text{Ti}$  retain their  $\text{MoSi}_2$  structure when they absorb hydrogen, but the insertion of hydrogen in the metal matrix causes highly anisotropic lattice changes; a large expansion along  $c$  and a small contraction in the  $a$  direction.<sup>16</sup>

In order to understand why  $\text{Ti}_2\text{Pd}$  forms a stable hydride in contrast with  $\text{Pd}_2\text{Ti}$ , the same  $\text{MoSi}_2$ -type structure for these hydrides was adopted in the calculations. The theoretically

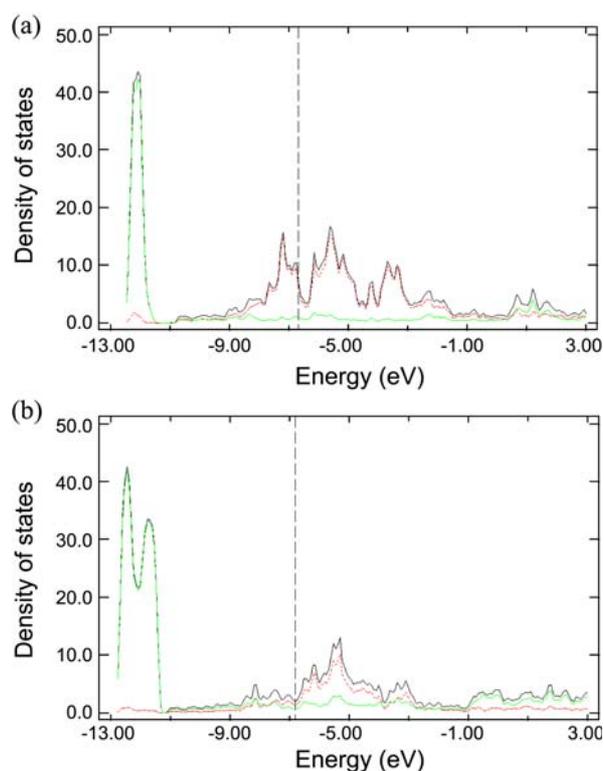
**Table 2.** Lattice constants  $a$  and  $c$  ( $\text{\AA}$ ) and atomic parameter  $z$  of Ti-Pd intermetallics. For  $\text{Ti}_2\text{Pd}$  and its hydride, Pd is in  $2a$  and Ti and H in  $4e$  positions. The Ti and Pd positions are exchanged in  $\text{Pd}_2\text{Ti}$  and its hydride.

Parameter	$\text{Ti}_2\text{Pd}$ <sup>13</sup>	$\text{Pd}_2\text{Ti}$ <sup>8</sup>	$\text{Ti}_2\text{PdH}_2$ <sup>16</sup>
$a$	3.09	3.24	2.85
$c$	10.054	8.48	12.508
$z$ (Ti)	0.333		0.3406
$z$ (Pd)		0.333	
$z$ (H)			0.8139

determined cell and structure parameters for the investigated compounds, along with the experimental values obtained from X-ray diffraction measurements, are given in Table 2.

## Results and Discussion

**Electronic Structure of the Intermetallic Compounds  $\text{Ti}_2\text{Pd}$  and  $\text{Pd}_2\text{Ti}$ .** We start with the pure intermetallics. The total and projected density of states (DOS) for  $\text{Ti}_2\text{Pd}$  and  $\text{Pd}_2\text{Ti}$  are shown in Figure 2. The Pd 4d states are found at low energies with the main peaks corresponding to rather localized states situated between  $-13$  and  $-11$  eV, while the Ti 3d states, which are more delocalized, result in a broad structure located at higher energies between  $-9$  and  $-1$  eV. This feature is reminiscent of the relative position of the atomic d levels. The Ti 3d and Pd 4d states are of course fairly mixed, and hybridized with metal s, p states. This



**Figure 2.** Total and projected DOS plots on Ti atoms (red line) and Pd atoms (green line) of (a)  $\text{Ti}_2\text{Pd}$  and (b)  $\text{Pd}_2\text{Ti}$  alloys. The Fermi level refers to the vertical dashed line.

mixing leads to a partly covalent character of the Ti-Pd bonds. The Ti to Pd charge transfer and the filling of the Pd d bands require that a late Pd atom has as many Ti atoms as its nearest neighbors as possible to facilitate the charge transfer and bonding interaction. The contribution of the Ti states at the Fermi level ( $E_F$ ) is larger than that of the Pd states. There are two common features in the DOS profiles for these compounds, indicating that the Pd 4d bands are fully occupied and the states near the Fermi level are mainly the broad Ti 3d bands. The bandwidth of the filled Pd d bands in  $Pd_2Ti$  is much wider than that of  $Ti_2Pd$ . This is due to the more Pd-Pd interactions between the metal atoms in the unit cell of  $Pd_2Ti$ .

Regarding the bonding, the COOP curves in Figure 3 show that a substantial part of Ti-Ti bonding states in  $Ti_2Pd$  is occupied at  $E_F$  (Fig. 3(a)), while in  $Pd_2Ti$  both the lower Pd-Pd bonding and the upper Pd-Pd antibonding states are well below  $E_F$  (Fig. 3(b)). Therefore, the Ti-Ti interaction in  $Ti_2Pd$  is much higher than Pd-Pd one in  $Pd_2Ti$ . The Ti-Pd, Ti-Ti, and Pd-Pd overlap populations are summarized in Table 3.

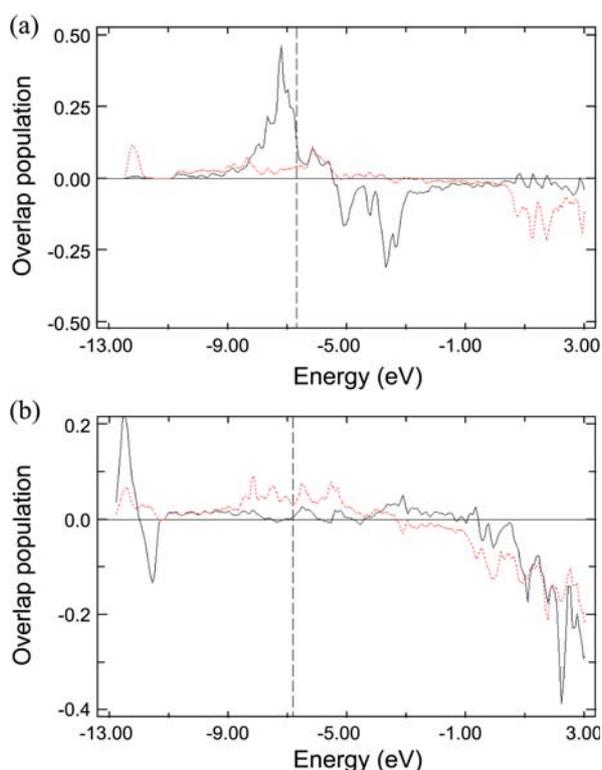
**Electronic Structure of the Hydrides  $Ti_2PdH_2$  and  $Pd_2TiH_2$ .** In Figure 4, we show the DOS profiles of  $Ti_2PdH_2$  and  $Pd_2TiH_2$ . One can see that absorption of hydrogen atoms within the host intermetallic lattices introduces new s bands associated with H atoms in the low-energy region (from  $-16.5$  to  $-14$  eV). The H s states have moderate mixing with the d states from the Ti and Pd atoms, reflecting the

**Table 3.** Overlap population (OP), charge, and distances for  $Ti_2Pd$  and  $Pd_2Ti$  alloys

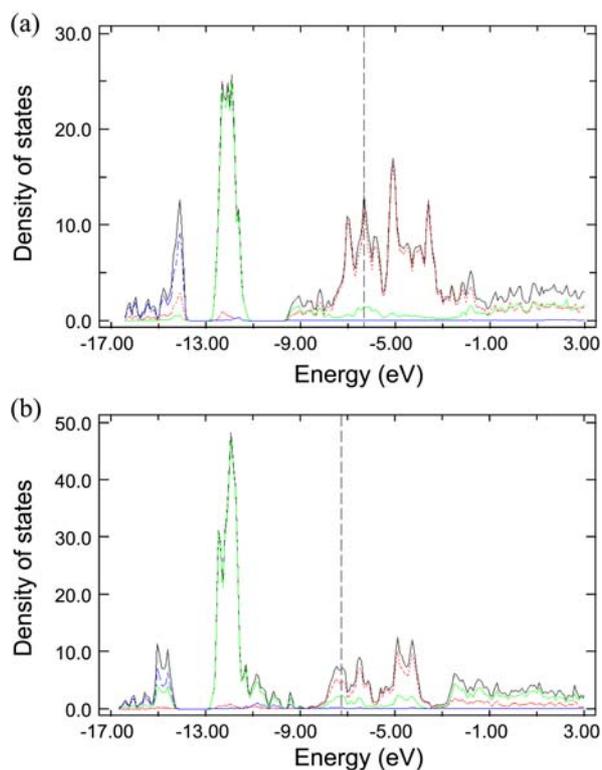
Compound	Atom or Bond type	Charge	OP	Distance (Å)
$Ti_2Pd$	Ti	0.61		
	Pd	-1.22		
	Ti-Ti		0.379	2.749
	Ti-Pd		0.170	2.755
$Pd_2Ti$	Ti	1.98		
	Pd	-0.99		
	Pd-Pd		0.098 <sup>a</sup>	2.689/2.832
	Pd-Ti		0.180 <sup>a</sup>	2.693/2.824

<sup>a</sup>OP: Average overlap population

hydrogen-metal interaction. This low-energy bonding states show a strong hydrogen character, while the corresponding high-energy antibonding states contain more pronounced Ti and Pd contributions. In both cases, a new structure associated with metal-hydrogen bonding states appears below the Pd 4d bands. For  $Ti_2PdH_2$ , they are mainly derived from the Ti-H interaction which leads to an important energy lowering of the Ti 3d states located above the Fermi level in the pure intermetallic  $Ti_2Pd$ , an important factor which is crucial to the stability of the hydride. In this hydride, the Ti-H interaction is strong enough to stabilize below  $E_F$  Ti d states that were mostly empty in the pure intermetallic compound. The contribution of Pd 4d to this bonding is very weak, even



**Figure 3.** COOP plots of (a)  $Ti_2Pd$  and (b)  $Pd_2Ti$  alloys: a Ti-Ti bond of  $Ti_2Pd$  and a Pd-Pd bond of  $Pd_2Ti$  (black solid line) and a Ti-Pd bond (red dotted line). The Fermi level refers to the vertical dashed line.



**Figure 4.** Total and projected DOS plots on Ti atoms (red line), Pd atoms (green line), and H atoms (blue line) of (a)  $Ti_2PdH_2$  and (b)  $Pd_2TiH_2$  hydrides. The Fermi level refers to the vertical dashed line.

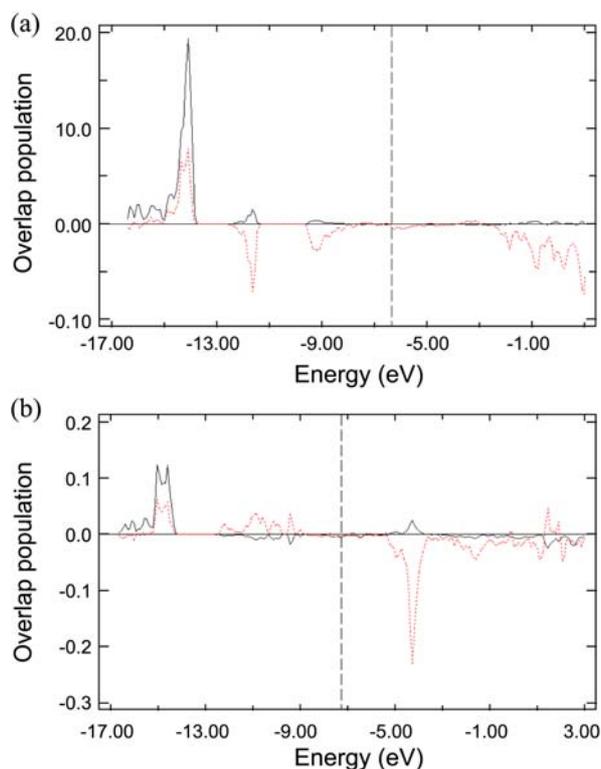
**Table 4.** Overlap populations (OP) for H-Ti and H-Pd bonds in  $\text{Ti}_2\text{PdH}_2$  and  $\text{Pd}_2\text{TiH}_2$ . BL denotes the bond length between two given atoms

Hydride	H-Ti		H-Pd	
	BL (Å)	OP	BL (Å)	OP
$\text{Ti}_2\text{PdH}_2$	2.042/1.932	0.128 <sup>a</sup>	2.327	0.002
$\text{Pd}_2\text{TiH}_2$	2.327	0.082	2.042/1.932	0.092 <sup>a</sup>

<sup>a</sup>OP: Average overlap population

though it is lower in energy than Ti 3d states, as shown in Figure 4. This is due to a very low coordination number of H with Pd in the octahedral sites.

In hypothetical  $\text{Pd}_2\text{TiH}_2$  the metal-hydrogen bonding states occur at lower energies than in  $\text{Ti}_2\text{PdH}_2$ , which seems to be favorable for hydride formation. However, as seen in Figure 5, these states are formed from the interaction of hydrogen with the lower lying Pd 4d states; the antibonding counterparts also lie below  $E_F$ . Therefore, there is no net gain in energy to stabilize the hydride. This is in contrast to the case of  $\text{Ti}_2\text{PdH}_2$  where mostly empty Ti 3d states in the pure intermetallic  $\text{Ti}_2\text{Pd}$  are lowered in energy to form metal-hydrogen bonding states. The most important difference observed in the bonding of H with Pd and Ti is that the Pd d states are already occupied in the pure intermetallic while a majority of the Ti d states are located above  $E_F$ . The occupation of metal-hydrogen antibonding states in hypothetical  $\text{Pd}_2\text{TiH}_2$  thus does not favor the hydride formation.

**Figure 5.** COOP plots for Ti-H (black solid line) and Pd-H (red dotted line) of (a)  $\text{Ti}_2\text{PdH}_2$  and for Pd-H (black solid line) and Ti-H (red dotted line) of (b)  $\text{Pd}_2\text{TiH}_2$ . The Fermi level refers to the vertical dashed line.

These results are in good agreement with the calculated energy of hydrogen absorption which is strongly endothermic (123.1 kJ/mol  $\text{H}_2$ ) for  $\text{Pd}_2\text{TiH}_2$ .<sup>16</sup>

To gain a deeper understanding of the interaction between the host metal atoms and H atoms, we performed a Mulliken population analysis of the  $\text{Ti}_2\text{Pd}$  and  $\text{Pd}_2\text{Ti}$  hydrides. The theoretical results are listed in Table 4. The overlap populations (OP) in Table 4 demonstrate that the average value for H-Ti bonds in  $\text{Ti}_2\text{PdH}_2$  is higher than that for H-Pd bonds in  $\text{Pd}_2\text{TiH}_2$ , reflecting the stabilizing effect of titanium-hydrogen bonding. H increases its bond strength when H is absorbed in Ti-rich octahedral sites. Typically, a high positive OP value indicates strong covalent interaction. The COOP curves in Figure 5 show the bonding/antibonding nature of the interaction in question. Interactions between H and metal atoms are taken into account. Most Ti-H interactions show a bonding character below  $E_F$  and push its antibonding states above the  $E_F$ . It is likely that this factor is important in determining the stability of the lattice with the interstitial H. Many Pd-H antibonding states wind up higher in energy than the Pd d-block states in the intermetallic, but still below the Fermi level after interaction with the H. These levels are populated. The result is that the Pd-H bonding is weakened, as attested to by the lower OP value (Table 4). It should be emphasized that negative Pd-H COOP occurs below  $E_F$ . This prevents effective bonding between Pd and H atoms at the octahedral interstitial sites with five Pd neighbors in  $\text{Pd}_2\text{TiH}_2$  and thus plays a role in anomalous absence of hydride formation in  $\text{Pd}_2\text{Ti}$ .

## Conclusion

In this study, we find that the difference in the H absorption properties of  $\text{Ti}_2\text{Pd}$  and  $\text{Pd}_2\text{Ti}$  is related to the presence of both bonding and antibonding combinations of new dominant metal-hydrogen interactions below  $E_F$  that is unfavorable to the formation of the hydride. This occurs in  $\text{Pd}_2\text{Ti}$ , while in  $\text{Ti}_2\text{Pd}$  the Ti-H bond interaction leads to the pushing of its antibonding states above the  $E_F$ . Only the bonding combination remains filled. It can be suggested that this metal-hydrogen bonding should play a role in the stability of the alloy. Our results illustrate why  $\text{Ti}_2\text{Pd}$  forms a stable hydride and  $\text{Pd}_2\text{Ti}$  does not.

**Acknowledgments.** This work was supported by the Kyungshung University Research Grant in 2011.

## References

- Schlapbach, L.; Züttel, A. *Nature (London)* **2001**, *414*, 353.
- Züttel, A. *Mater. Today* **2003**, Sept. 24.
- Ros, D. K. *Vacuum* **2006**, *80*, 1084.
- Crabtree, G. W.; Dresselhaus, M. S. *MRS Bull.* **2008**, *33*, 421.
- Lynch, F. E. *J. Less-Common Met.* **1991**, *172-174*, 943.
- Maeland, A. J.; Libowitz, G. G. *J. Less-Common Met.* **1980**, *74*, 295.
- Bowman, R. C.; Attalla, A., Jr.; Abell, G. C.; Cantrell, J. S.; Maeland, A. J. *J. Less-Common Met.* **1991**, *172-174*, 643.

8. Krautwasser, P.; Bahn, S.; Schubert, S. Z. *Metallkd.* **1968**, 59, 724.
  9. Wodniecki, P.; Wodniecka, B.; Kulinska, A.; Uhrmacher, M.; Lieb, K. P. *J. Alloys Compd.* **2004**, 385, 53.
  10. Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, 100, 6093.
  11. Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. A* **1979**, 366, 23.
  12. Ren, J.; Liang, W.; Whang, M.-H. *CAESAR Program*; PrimeColor Software Inc.: Cary, NC, 1998.
  13. Nevitt, M. V.; Downey, J. W. *Trans. Met. Soc. AIME* **1962**, 224, 195.
  14. Lundin, C. E.; Lynch, F. E.; Magee, C. B. *J. Less-Common Met.* **1977**, 56, 19.
  15. Westlake, D. G. *J. Less-Common Met.* **1983**, 91, 1, and references cited therein.
  16. Chen, X.-Q.; Fu, C. L.; Morris, J. R. *Intermetallics* **2010**, 18, 998.
-