

Electronic structure and $B2$ phase stability of Ti-based shape-memory alloys

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In order to further search a correlation between electronic structure and the $B2$ phase stability of TiM binary alloys with $M=Fe, Co, Ni, Pd, Pt, Au, Cu,$ and Ag , we perform a first-principles calculation using a tight-binding linear muffin-tin orbital method. A "correlation parameter" of the density of states (DOS) of electron, which reflects the shape properties of DOS, is introduced. It is found that using the parameter coupling the overlapping occupancies of DOS's and lattice constants, the phase stability of the $B2$ structure in these alloys can be described very well. Our conclusions are also confirmed by a comparison with the difference charge-density map. In addition, the temperatures of Martensitic phase transformation of these alloys are calculated and are found to be comparable with the experimental. [S0163-1829(99)07347-6]

I. INTRODUCTION

In the last few decades, shape-memory alloys have found widespread applications in the fields of engineering and medicine. The shape-memory effect of these materials is related to a reversible Martensitic transformation, which is a type of nondiffusive structure phase transformation involving a change in the shape of the unit cell together with atomic scale displacements of positions of the atoms in the lattice. In this effect, the study of phase stability has been an interesting subject. Though, a lot of theoretical and experimental works have been devoted to interpreting the phenomenon, a more detailed microscopic picture is generally lacking and needed. This situation is true in Ti-based shape-memory alloys.

It is well known that the $B2$ structure of TiM with $M=Ni$ is maintained until near room temperature, while for the isoelectronic analogous $M=Pd$ or Pt , this structure exists only at temperatures higher than 900 K. On the other hand, when M stands for transition metals, Co or Fe , the Martensitic $B2-B19$ (or $B19'$) transformations temperature, M_s of $TiCo$ is about 40 K and $TiFe$ is stable in $B2$ phase until 0 K. Moreover, the Martensitic phase transformation even occurs at a higher temperature in $TiAu$ than in $TiPd$ and $TiPt$. Despite the fact that Cu and Ag are isoelectronic to Au , $TiCu$ and $TiAg$ do not exist in the $B2$ structure at all. These phenomena have attracted much attention from both experimental and theoretical works.¹⁻⁶

Eibler, Redinger, and Neckel carried out a calculation for

$TiFe$, $TiCo$, and $TiNi$. They attributed the instability of the $B2$ structure to the increasing occupation of the antibonding states.¹ Several electronic structure calculations have also been carried out for $TiFe$,² $TiNi$,³ and $TiPd$ (Ref. 4) compounds. Shabalovskaya *et al.* did systematically experimental and theoretical works for these TiM alloys, and they emphasized that the $B2$ phase stability was strongly correlated with the $d-d$ and $d-p$ bonds between Ti and M in these Ti-based intermetallics.⁵ But this description was ambiguous sometimes. Recently, Ye and co-workers tried to illustrate the phenomenon more clearly by a theoretical calculation. They calculated the overlapping occupancies (the number of common electrons) between partial density of states (DOS's), and their numerical calculations supported the above opinion. They, however, failed to interpret that $TiAu$ is more stable than $TiCu$ in the $B2$ phase.⁶ In fact, the $B2$ $TiCu$ was not observed experimentally while $B2$ $TiAu$ existed. Moreover, they also found that the $B2$ phase stability of $TiPt$ did not follow their interpretation. They gave a comment that the $B2$ phase stability was controlled by many kinds of factors, and only part of these factors were considered in their works. In fact, using the number of electrons to explain the phase stability is somewhat careless. As is well known, if bond A is longer than bond B , bond A may be weaker than bond B even if there are more electrons at bond A than at bond B . Therefore, one should use the electron density rather than the number of electrons to explain the phase stability. Likewise, the shape factor of DOS's was not considered in their calculations. In the present paper, the $B2$

TABLE I. The WS ratio r_{Ti}/r_M from experimental values and calculated equilibrium lattice parameters a_0 of TiM alloys.

	M							
	Fe	Co	Ni	Pd	Pt	Au	Cu	Ag
r_{Ti}/r_M	1.14	1.16	1.17	1.06	1.05	1.01	1.14	1.01
a_0 (a.u.)	5.677	5.687	5.727	6.044	6.073	6.154	5.831	6.163

phase stability of TiM with $M = \text{Fe, Co, Ni, Pd, Pt, and Au}$, together with two other compounds TiCu and TiAg with hypothetical $B2$ structure, is studied once again on the basis of *ab initio* results. The numerical calculations are performed using tight-bonding linear muffin-tin orbital (TB-LMTO) method.⁷⁻⁹ Our purpose is to further explore the mechanism of $B2$ phase stability in these Ti-based shape-memory alloys. We introduce a correlation parameter of DOS's coupling electron occupancies and lattice constant to describe the $B2$ phase stability of TiFe, TiCo, TiNi, TiPd, TiPt, TiAu, TiCu, and TiAg. The parameter may reflect the shape property of DOS and the overlapping occupancies between partial DOS's. Using the parameter, the phase stability of the $B2$ structure in these alloys can be described very well. The present paper overcomes the problem of Ye and co-workers of explaining the phase stability of $B2$ of TiPt and TiCu alloys.

The general arrangement of the paper is as follows. In Sec. II we describe the theoretical and numerical method. In Sec. III in its former part we present some numerical results, and in its latter part the shape factor (correlation parameter) and $B2$ phase stability are discussed in detail. Meanwhile the physics picture behind the present method is also illustrated. And, finally, in Sec. IV are the conclusions.

II. COMPUTATION METHOD

In the present paper, we perform self-consistently scalar relativistic calculations using TB-LMTO method, where the

atom sphere approximation (ASA) and the local spin-density approximation¹⁰ are used. The exchange and correlation potential is from Ceperley and Alder;¹¹ "combined correction" is taken into account, and the density of state is calculated with tetrahedron method.¹² In the calculations, the maximum angular momenta l_{\max} describing the wave functions is chosen as $l_{\max}=2$ for all atoms, and the corresponding atomic wave functions construct a minimal basis set. For all the other electrons, a frozen-core approximation is adopted, i.e., their wave functions are assumed to be the atomic wave functions and are not iterated. A fully relativistic atomic program is used to generate this core density. Wigner-Seitz (WS) radii are determined by considering the atomic radii ratio for all constituent atoms (see Table I) and 165 k points are used in the irreducible wedge of the cubic Brillouin zone. Nonpolarized calculations are carried out for equiatomic compounds TiM with $B2$ structure and $M = \text{Fe, Co, Ni, Pd, Pt, Au, Cu, and Ag}$.

III. RESULTS AND DISCUSSIONS

A. Numerical results

From the experimental side, we have known that along the sequence of the alloys (TiFe-TiCo-TiNi-TiPd-TiPt-TiAu-TiCu and TiAg) the stability of the $B2$ phase decreases.⁵ On the basis of the calculations of electronic structure, one scheme to study phase stability is to analyze the density-of-state curves of electronic structure. In order to obtain these DOS curves, we first calculate the total energy of $B2$ TiM alloys for various lattice constants to determine their equilibrium lattice parameters. The minimum in the curves (not shown here) gives the predicted equilibrium lattice constants. The results are listed in Table I. Using the equilibrium lattice parameters we calculate the electronic structure of these alloys. The corresponding total DOS's, d , p , and s partial, are shown in Figs. 1-4, respectively.

First, from Fig. 1 we see that for TiFe, TiCo, TiNi, TiPd, TiPt, and TiAu their Fermi levels fall on a local minimum (a

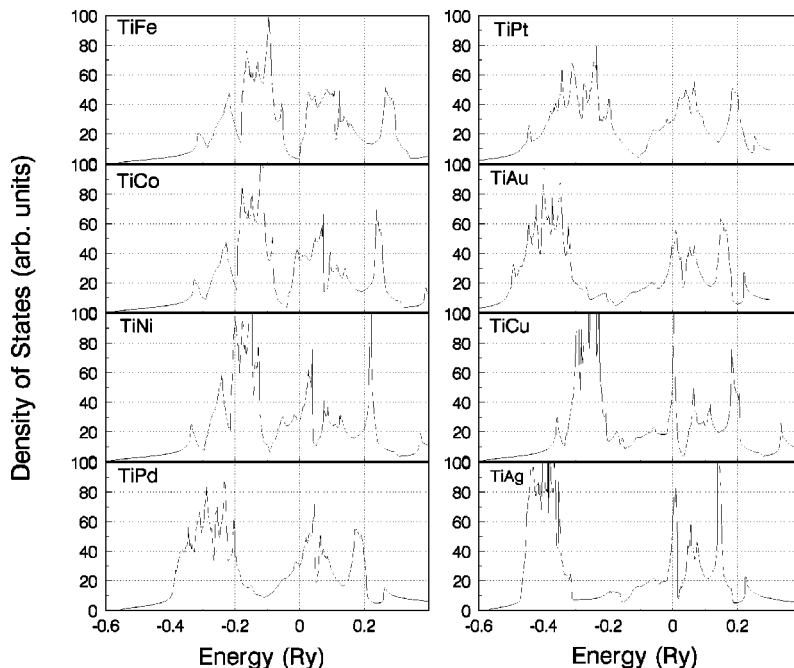


FIG. 1. The total DOS curves of TiM with $M = \text{Fe, Co, Ni, Pd, Pt, Au, Cu, and Ag}$. The Fermi level is at the value of 0 Ry.

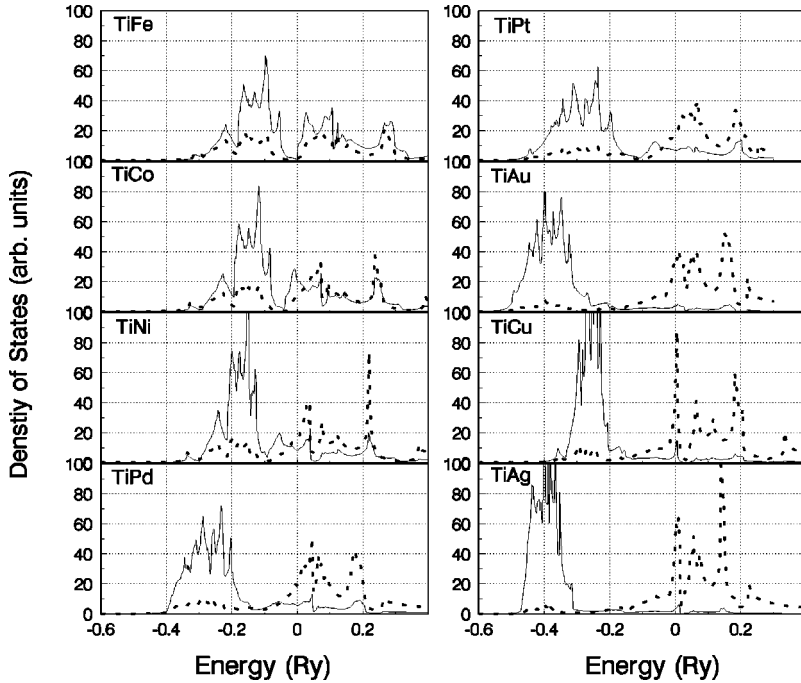


FIG. 2. The d -partial DOS curves of Ti M with M =Fe, Co, Ni, Pd, Pt, Au, Cu, and Ag, where the solid line and dotted line denote the d -partial DOS of M site and Ti site, respectively. The Fermi level is at the value of 0 Ry.

dip) of a DOS curve while for TiCu and TiAg such a dip does not exist at all. Note that the latter are not experimentally observed as a $B2$ phase. As well known, a dip is generally considered to divide a DOS into a bonding state and an antibonding state; thus, when a Fermi level falls on the dip, the corresponding structure may be regarded as a save-energy system, as compared with one whose Fermi level does not fall on the dip. Thus, this kind of structure is more stable; otherwise, it is unstable. From this analysis, it may not be difficult to understand that TiAg and TiCu are unstable and are not experimentally observed in a $B2$ phase.

Now, let us focus our attention on the total DOS value at Fermi level [$N_T(E_F)$] in Fig. 1. These $N_T(E_F)$'s are also listed in Table II for all these alloys. From the table, we find that though the most stable $B2$ alloy TiFe, that is, the one with the lowest Martensitic transformation temperature (M_s), has the lowest DOS value $N_T(E_F) = 11.73$, a clear fact is that higher stability does not correspond to lower DOS value at the Fermi level. Obviously, TiPt has lower DOS value than TiNi and TiPd have (Table II) while TiNi and TiPd are more stable than TiPt in the $B2$ structure. The same situation also occurs in TiCo, TiNi, and TiPd. TiCo is more stable than TiNi and TiPd in the $B2$ phase, but TiCo has a larger DOS value at Fermi level than TiNi and TiPd (Table II). A similar calculation has been given in Ref. 6. From Table II of Ref. 6, it can also be seen obviously that TiCo has a larger DOS value at Fermi level than TiNi and TiPd, and TiPt has a lower DOS value at Fermi level than TiPd and TiNi. This seems to be puzzling. Common knowledge is that the lower $N_T(E_F)$ is, the more stable the phase is.¹⁵ In fact, this is not surprising. Experimental and theoretical works have found that the d - d and d - p hybridization between Ti and M atoms are the main cause of $B2$ phase stability in these Ti-based intermetallics.^{5,6} But a physical picture behind this is still required.

Before we interpret this point, we look into the partial DOS values at Fermi level at the site of the constituent elements. The results, along with the corresponding electron

occupancies of partial DOS, are listed in Table II. From Table II we find that, except for that of TiPt and TiCu, the d -partial DOS value at Fermi level [$N_d(E_F)$] of Ti reduces monotonously from 1.56 in TiFe to 50.82 in TiAg. This trend also occurs in p -partial DOS value at Fermi level [$N_p(E_F)$] of Ti site in Ti M alloys. Furthermore, nearly the same results can be seen in the electron occupancies of d -partial DOS (or p -partial DOS) n_d (or n_p) for Ti site in Ti M compounds. But, in M site, these phenomena are not observed for $N_d(E_F)$ and $N_p(E_F)$, and n_p , except for n_d .

The other interesting results can also be seen in Fig. 2, for instance, except for TiCu when going from TiFe to TiAg, the main part of the bonding state of d electrons at M sites gradually moves toward the bottom of the valence band while the antibonding state of d electrons at Ti sites becomes gradually strong. This may reflect the gradual weakening of d - d bonds between Ti and M . We return to Fig. 1 again. It is evident that there exists a double-peak structure in all the total DOS's of these Ti-based compounds. For TiFe, the double-peak structure is the most typical two-peak structure, in which the Fermi level falls on the pseudogap of the DOS curve. This indicates that all the bonding states are filled with electrons, and all the antibonding states are left empty; therefore, the strong bonding effect occurs. This follows the conclusion of Dalton and Deegan that in a bcc metal the bcc phase stability is closely related to a double-peak structure of DOS.¹⁴ In fact, in these alloys, the shapes of DOS in TiCo and TiNi are more similar to that in TiFe than those in the other Ti-based alloys: TiPd, TiPt, TiAu, TiCu, and TiAg. Therefore, Ti M , where M is transition metal Co, Ni may be more stable than those where M is noble metals Au, Cu, and Ag and transition metals Pd and Pt. All the above numerical results are in agreement with ones from Ref. 6 or Ref. 5.

By comparing Figs. 1, 2, 3, and 4, we find that the double-peak structure mentioned above is produced by d - d hybrid, and the dip on which Fermi level falls is formed mainly by d - d and d - p hybrid in these alloys. In particular, the dips of

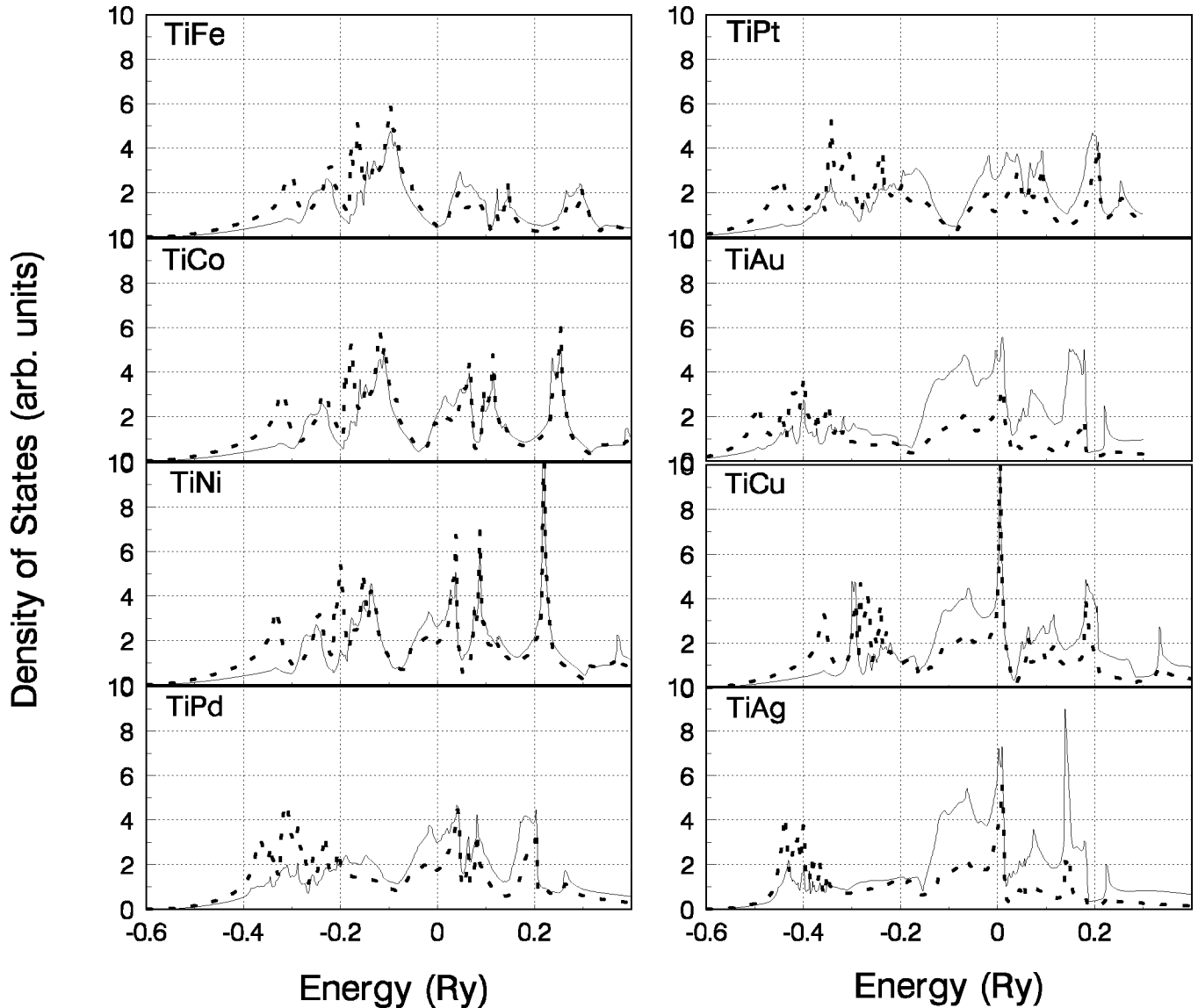


FIG. 3. The p -partial DOS curves of $\text{Ti}M$ with $M = \text{Fe}, \text{Co}, \text{Ni}, \text{Pd}, \text{Pt}, \text{Au}, \text{Cu},$ and Ag , where the solid line and dotted line denote the p -partial DOS of M site and Ti site, respectively. The Fermi level is at the value of 0 Ry.

TiFe, TiCo, and TiNi are mainly due to the hybrid of d - d bond between Ti and Co, Fe, and Ni, while the dips of TiPd, TiPt, and TiAu are produced by d and p electrons between Ti site and Pd, Pt, and Au site. From Figs. 2, 3, and 4, we notice that the contribution of s -partial DOS to interbonding state is negligible because its bond peak is further from Fermi level than corresponding p -partial and d -partial DOS's.

B. Shape factor and $B2$ phase stability

The above numerical calculations show indeed some correlation between the electron structure and $B2$ phase stability. Now we explain them using a correlation parameter of DOS's coupling their overlapping occupancies and lattice constants. The overlapping occupancies of DOS's have been used in Ref. 6. It denotes the number of common electrons in two different partial DOS's. Using the overlapping occupancies, Ye and co-workers explained the $B2$ phase stability of these alloys, but they gave an errors prediction that TiCu was more stable than TiAu in $B2$. They also did not interpret the

phase stability of TiPt alloy. This may be due to the shape characters of DOS's not being considered in their works. In addition, they suggested using the number of electrons to explain the phase stability, which is somewhat careless. More accurately, one should use the electron density to explain the stability.

Now we illustrate that the shape factor of DOS is also important to determine the phase stability. In order to understand this point more clearly, we present a simple example in Fig. 5(a) and 5(b). In Fig. 5(a), there are two DOS curves, each of which is simply assumed as a square shape. Such two DOS curves overlap partly and have an overlapping area of S_a . In Fig. 5(b), DOS's are a copy from the DOS's in Fig. 5(a), but they have higher DOS value than respective DOS curves of Fig. 5(a) and have overlapping area S_b . If $S_a = S_b$, we may know that the energy of overlapping region is lower in Fig. 5(a) than in Fig. 5(b). Therefore, if an alloy has the DOS curves of Figs. 5(a) or 5(b) and its phase stability is controlled by the overlapping of the DOS's, the alloy is more stable with the DOS's of Fig. 5(a) than with the DOS's of

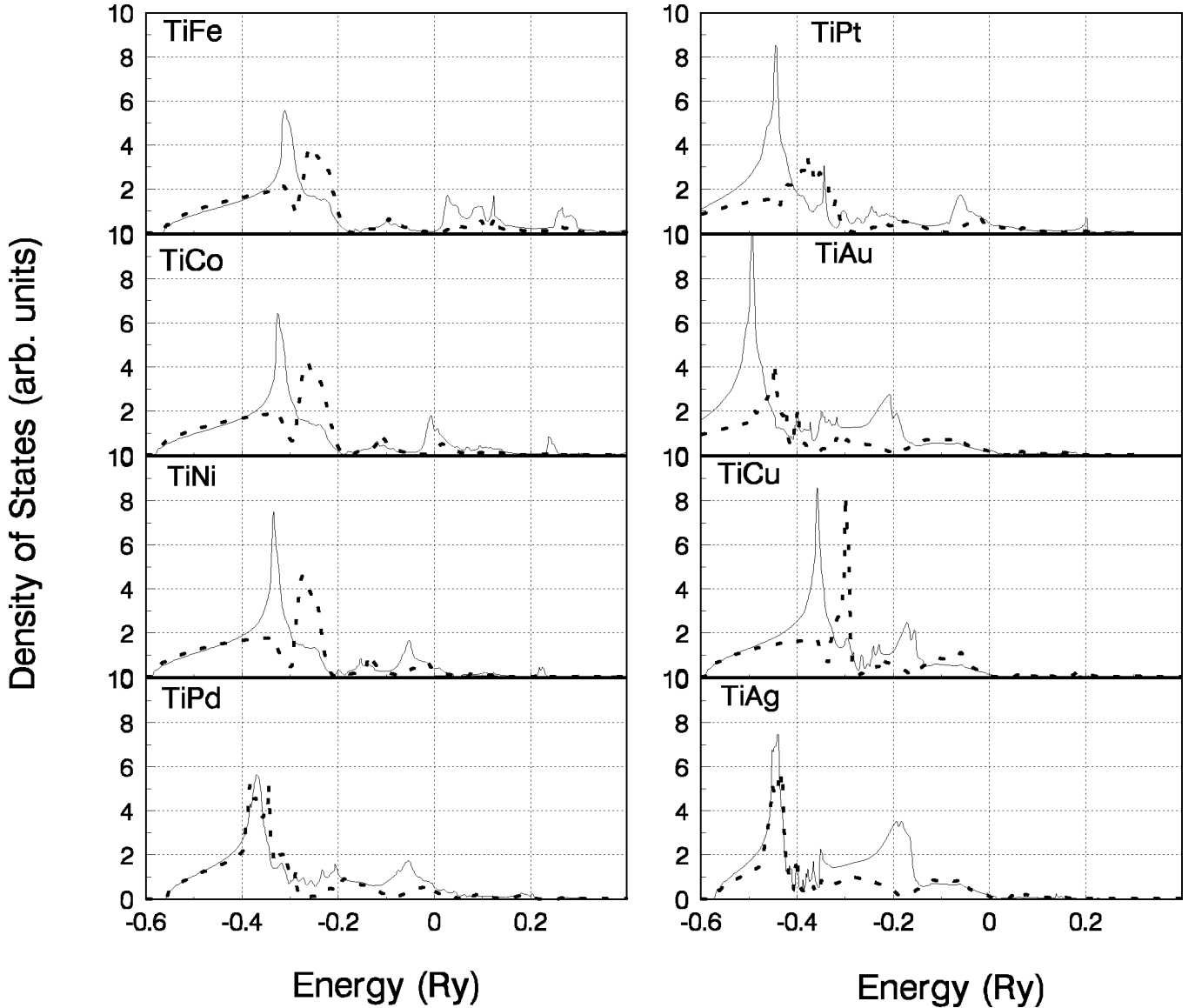


FIG. 4. The s -partial DOS curves of TiM with $M = \text{Fe, Co, Ni, Pd, Pt, Au, Cu, and Ag}$, where the solid line and dotted line denote the s -partial DOS of M site and Ti site, respectively. The Fermi level is at the value of 0 Ry.

Fig. 5(b). But, if phase stability is determined by only overlapping area, a conclusion can sincerely attain that the stability of the alloys is the same for Fig. 5(a) and Fig. 5(b). Thus, from such a simple example, we can conclude that it is necessary to consider the effect of the shape of the DOS curve on phase stability. We define such a correlation parameter (or shape factor) of DOS curves, and it has the following form:

$$C_p = \frac{\int_{E_F}^{E_F} g_1(E)g_2(E)dE}{g_{1 \max}g_{2 \max}}, \quad (1)$$

where E is energy, $g_1(E)$ and $g_2(E)$ are two DOS functions from first-principles calculations, and $g_{1 \max}$ and $g_{2 \max}$ are the maximum DOS values of $g_1(E)$ and $g_2(E)$ below Fermi level (E_F), respectively. Obviously, using Eq. (1), we can explain the results from Fig. 5. We now calculate the overlapping occupancies between p - d DOS's and d - d DOS's and corresponding correlation parameter C_p 's between Ti site

and M site in TiM alloys. The results are listed in Table III. From Table III we see that, roughly, the overlapping area decreases gradually when going from TiFe to TiAg for d - d hybridization and also for the hybrid of the d -partial DOS in M site and p -partial DOS in Ti site (M_d - Ti_p). For the hybrid of the d -partial DOS in Ti site and p -partial DOS in M site (Ti_d - M_p), the trend is approximately inverse to the one of d - d (or M_d - Ti_p) hybridization.

As compared with the results of overlapping occupancies from Ye and co-workers, we find that the present results of d - d and Ti_d - M_p are in agreement with their data (see Table V in Ref. 6). But they did not perform a calculation for M_d - Ti_p . They believed that the centers of Ti_d and M_p were more energetically close to each other than the centers of Ti_p and M_d ; thus the term of Ti_p - M_d was negligible as compared with one of the Ti_d - M_p . In fact, the term of M_d - Ti_p has more contribution to overlapping occupancies than the one of Ti_d - M_p . This can be seen in our Table III. Therefore, the difference between the centers of two bands may not be a

TABLE II. The DOS value at Fermi level [$N_T(E_F)$, $N_d(E_F)$, $N_p(E_F)$, and $N_s(E_F)$] and occupancies of d , p , s electrons (n_d , n_p , and n_s) in TiM alloys.

	M							
	Fe	Co	Ni	Pd	Pt	Au	Cu	Ag
$N_T(E_F)$	11.73	34.33	28.28	30.51	28.12	43.13	70.06	64.42
$N_d(E_F)$ of Ti	1.56	9.34	17.55	19.14	16.54	32.00	51.90	50.82
n_d of Ti	2.5662	2.5535	2.5285	2.4182	2.4739	2.4012	2.4898	2.3176
$N_d(E_F)$ of M	9.10	19.83	8.48	5.73	6.87	3.78	8.36	3.28
n_d of M	6.5575	7.5301	8.5082	8.6232	8.2844	9.1873	9.3783	9.4684
$N_p(E_F)$ of Ti	0.51	1.63	1.89	1.76	1.27	2.43	4.47	3.57
n_p of Ti	0.9085	0.9064	0.8849	0.8264	0.9057	0.7852	0.8211	0.7169
$N_p(E_F)$ of M	0.44	2.11	2.62	3.01	2.71	4.53	5.13	6.45
n_p of M	0.6541	0.6433	0.6838	0.7239	0.7893	1.0258	0.8284	0.9946
$N_s(E_F)$ of Ti	0.036	0.307	0.341	0.347	0.355	0.191	0.087	0.114
n_s of Ti	0.6655	0.6634	0.6612	0.6317	0.6194	0.5497	0.6229	0.5530
$N_s(E_F)$ of M	0.090	1.078	0.398	0.527	0.436	0.191	0.126	0.158
n_s of M	0.6387	0.6861	0.7442	0.7707	0.9272	1.0779	0.8497	0.9293

good method to determine the contribution of the bands to interbonding state. Also, the close degree of the two centers of two bands can be reflected roughly in our correlation parameter. In Table III, we see that the correlation parameters of Ti_d-M_d (C_{p1}) are larger than those of Ti_p-M_d (C_{p3}) and smaller than those of Ti_d-M_p (C_{p2}) for TiFe, TiCo, and TiNi, while C_{p3} is larger than C_{p1} and smaller than C_{p2} for TiPd, TiPt, and TiAg. Our numerical results also show that similar results can be also obtained in the difference of the two corresponding centers of these bands for these alloys. Furthermore, we also calculate the correlation parameter of p - s and d - s partial DOS's between Ti and M sites and find that they are smaller than corresponding ones of d - d and d - p partial DOS's by a factor of, approximately, 2–4. This is reasonable. From Fig. 2–4, we can find d - (or p -) and s -partial DOS's have less overlap than d - p DOS's.

In order to do a more detailed comparison with Ye and co-workers' results, we now add the overlapping occupancies of Ti_d-M_p (n_2) to the overlapping occupancies of M_d-Ti_d (n_1). We see the present results are identical to the

ones of Ye and co-workers (see Table III in Ref. 6), i.e., TiPt has more overlapping occupancies than TiPd and TiCu does than TiAu. However, if we add the term of M_d-Ti_p (n_3) to n_1 and n_2 , we find that TiPt has even more overlapping occupancies than TiCo though TiCu is more close to TiAu (see Table III). Therefore, if the overlapping area is solely one factor to determine the $B2$ phase stability in TiM intermetallics, this will lead to a poor prediction on the $B2$ phase stability of TiCu and TiPt. Fortunately, this situation may be improved by considering the shape factor of DOS and lattice constant. From Table III, we see that for d - d hybridization the shape factor (correlation parameter) C_{p1} decreases gradually when going from TiFe to TiAg except for TiPt. For d - p hybrid, this trend is not obvious. We assume that the phase stability is directly proportional to the shape factor multiplied by the overlapping areas, we calculate $n_1 * C_{p1} + n_2 * C_{p2} + n_3 * C_{p3}$, and the results ($n_i * C_{pi}$) are reported in Table III. Note that C_{p1} , C_{p2} , C_{p3} express the shape factor (correlation parameter) of Ti_d-M_d , Ti_d-M_p , and M_d-Ti_p , respectively. It is seen that when going from TiFe to TiAg the $n_i * C_{pi}$'s follow the trend of the $B2$ phase stability except for TiPt. But TiPt has some improvement, compared with $n_1 + n_2 + n_3$. In the present paper we also consider that the $B2$ phase stability is inverse to the cube of lattice constant. Because the smaller the cube of lattice constant is, the larger the electron density at d - d (d - p) overlapping region is. Considering this factor, we find the phase stability of TiPt is almost in agreement with the $B2$ phase stability of TiPd (see Table III). This is a great improvement because when one considers solely the factor of overlapping occupancies, TiPt is even more stable than TiCo in the $B2$ phase (see Table III). Likewise, TiCu follows the $B2$ phase stability sequence of these TiM compounds in the present calculations as the shape factor of DOS is considered. It should be stressed that in the present paper TiPt is predicted to be more stable than TiPd in $B2$ structure; perhaps, this attributes to the theoretical limit of TB-LMTO method. In our paper, except for a_0 , almost all factors, such as C_p , n_i , interbonding bandwidth, the DOS value at Fermi level, and the difference of band center, are more beneficial for $B2$ phase stability of TiPt than for that of TiPd.

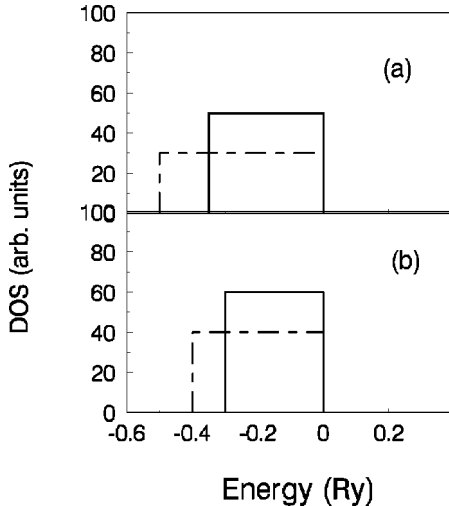


FIG. 5. A model of DOS curves (a) versus (b). The Fermi level is at the value of 0 Ry.

TABLE III. The overlapping occupancies n_i and correlation parameter C_{pi} (shape factor), where Ti_d , Ti_p , M_d , and M_p denote the d -partial DOS and p -partial DOS of Ti site and M site in TiM compounds, respectively.

	M							
	Fe	Co	Ni	Pd	Pt	Au	Cu	Ag
n_1 of Ti_d-M_d	2.5058	2.4651	2.3888	2.0488	2.2696	1.2641	1.4656	0.8873
n_2 of Ti_d-M_p	0.6270	0.6213	0.6680	0.7053	0.7713	0.9947	0.8093	0.9502
n_3 of Ti_p-M_d	0.8292	0.8059	0.7870	0.8112	0.8742	0.7754	0.7643	0.6693
C_{p1} of Ti_d-M_d	0.0595	0.0544	0.0506	0.0397	0.0505	0.0130	0.0065	0.0055
C_{p2} of Ti_d-M_p	0.0683	0.0624	0.0761	0.0653	0.0781	0.0417	0.0251	0.0245
C_{p3} of Ti_p-M_d	0.0519	0.0480	0.0420	0.0614	0.0564	0.0567	0.0271	0.0039
$C_{pi}^*n_i$	0.2350	0.2115	0.2049	0.1772	0.2102	0.1019	0.0506	0.0540
$C_{pi}^*n_i/a_0^3(10^{-3})$	1.162	1.150	1.091	0.803	0.932	0.437	0.252	0.231
$n_1+n_2+n_3$	3.9620	3.8923	3.8638	3.5653	3.9151	3.0342	3.0392	2.5068
n_1+n_2	3.1328	3.0864	3.0568	2.7541	3.0409	2.2588	2.2749	1.8375
n_1+n_2 (Ref. 6)	3.203	3.194	3.110	2.771	2.991	2.333	2.372	1.933
T_M	0.0	40.0	237	1197	767	2416	3033	3103
T_M (Ref. 5)	0.0	40.0	<300.0	>900.0	>900.0	>900.0		

A difference charge-density map may also confirm our results. The different charge density is the difference between the self-consistent solid-state charge density obtained at our calculation for equilibrium lattice constant and the superposed atomic charge density at the same lattice constant. We plotted these contours for the cases of TiAu and TiCu. The resulting Figs. 6(a) and 6(b) clearly show a stronger bonding charge density between Au atom and Ti atom in TiAu than one between Ti atom and Cu in TiCu compound. Our contour maps also suggest that the strongest interbonding occurs between Ti atom and Fe atom in TiFe of these TiM alloys (not shown here). All the results are in agreement with ours and support our present proposal.

It should be emphasized, as pointed out by Foiles¹⁵ and Carlsson, Fedders, and Myles,¹⁶ that the shape of DOS is important in determining the phase stability of different crystal structure with partially filled d bands. It can be also applied to the case of noble metals.¹⁷ On the root of the point of view from Foiles¹⁵ and Carlsson, Fedders, and Myles,¹⁶ the band energy can be described as the bandwidth with a coefficient that depends on the shape character of DOS. The coefficient, which reflects the shape character of DOS, is defined as a function of the fourth moment of DOS, and the moment is designed from an empirical function.^{15,16} The present method is equivalent to these models, but the shape factor is calculated directly from DOS curve based on the results of the first principles. The effect of shape of DOS on directional bond have also been illustrated by the fourth moment of DOS in Ref. 18.

Finally, it is interesting to estimate the temperature of Martensitic phase transformation of these TiM intermetallics. This can be simply realized by calculating the difference between $C_{pi}n_i/a_0^3$'s. If we assume that this difference of TiFe and TiCo corresponds to a value of 40 K, which is the M_s of TiCo, we can obtain the M_s of the other alloys by the following formula:

$$T_M = 40.0 \frac{(C_{pi}n_i/a_0^3)_M - (C_{pi}n_i/a_0^3)_{Fe}}{(C_{pi}n_i/a_0^3)_{Co} - (C_{pi}n_i/a_0^3)_{Fe}}, \quad (2)$$

where subscript M stands for Fe, Co, Ni, Pd, Pt, Au, Cu, and Ag, and T_M expresses M_s of TiM alloy. The present numerical results are listed in Table III. From the table we see that the T_M (M_s) of these alloys are comparable with the respective experimental values, but the value of TiAu is exceedingly larger than the experimental. This is not surprising that this model is very simplified. We also notice that the M_s of TiCu and TiAg are far larger than the ones of the other alloys. This is understandable that TiCu and TiAg do not exist in a $B2$ structure.

IV. SUMMARY

We performed TB-LMTO calculations to study the electronic structural properties and $B2$ phase stability of TiM ,

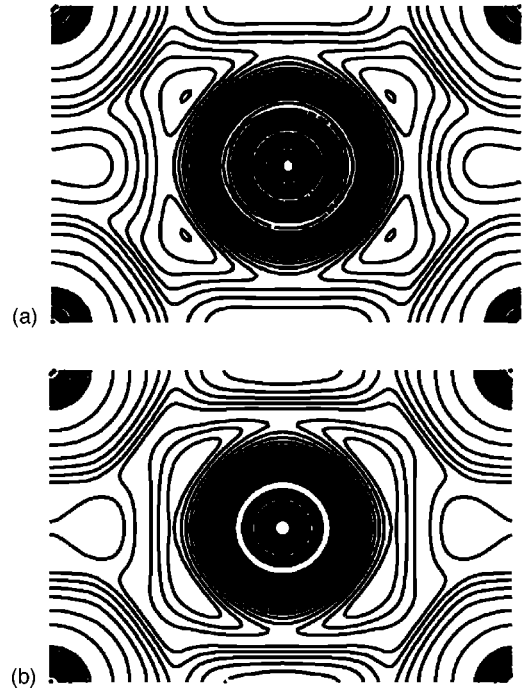


FIG. 6. Difference charge densities for (a) TiAu and (b) TiCu in (110) plane. The M atom at the center and Ti atoms at the corners.

where $M = \text{Fe, Co, Ni, Pd, Pt, Au, Cu, and Ag}$. We calculated the total and partial DOS values at Fermi level, we also calculated the electron number of partial DOS's, and we found the results were in agreement with the previous LMTO-ASA calculations.⁶ It was found that not only the overlapping occupancies but also shape factors of d - d and p - d partial DOS's governed the $B2$ phase stability of Ti-based compounds. Moreover, the lattice constant was also related to the $B2$ phase stability. Our conclusions were further confirmed by a comparison with the difference charge-density map. The present calculations resolved the problem of Ye and co-workers for explaining the $B2$ phase stability

of TiPt and TiCu alloys and developed a method to describe phase stability. Finally, the temperatures of Martensitic phase transformation of these alloys were estimated, and the results were comparable with the experimental.

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