Full-potential electronic structure of Ti$_2$AlC and Ti$_2$AlN

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Electronic structures of the hexagonal Ti$_2$AlC and Ti$_2$AlN compounds with Cr$_2$AlC-type structure calculated within the full-potential linearized augmented plane-waves formalism are presented. Geometrical optimization of the unit cell are in good agreement with experimental data. The analysis of the site and momentum projected densities of states shows that bonding is due to Ti d-C p (or Ti d-N p) and Ti d-Al p hybridizations. It is found that the intensity of the total density of state at Fermi level is higher for Ti$_2$AlN that has also a higher electrical conductivity. Results are compared to a recent work by Zhou and Sun[1] who assume a different crystal structure.

I. INTRODUCTION

Various experimental studies have shown[2–5] that Ti$_2$AlC and Ti$_2$AlN crystallize under the Cr$_2$AlC or Hägg phase (H-phase) structure identified by Jeitschko *et al.* in 1963 from x-ray diffraction experiments on Cr$_2$AlC crystals. The space group is $P6_3/mmc$ and the Wyckoff positions are $4f$ for Ti, $2d$ for Al, and $2a$ for C or N. The structure has been confirmed since several times by other techniques.[6] In a recent work, Zhou and Sun[1] employed $4f$ and $2a$ positions for Ti and the metalloid (C or N), respectively, but used the $2c$ position for Al. Apparently similar, the $2d$ [(1/3, 2/3, 3/4) , (2/3, 1/3, 1/4)] and $2c$ positions [(1/3, 2/3, 1/4), (2/3, 1/3, 3/4)] are[7] actually quite different. In fact, each of the $2d$ and $2c$ positions corresponds to a different stacking of the metals along the c direction. If one does not consider the metalloid, the stacking of the metals in the correct H phase is the classical $ABAB$ sequence of an hcp metal with a two planes periodicity along the hexagonal axis. The chemical sequence is formed by two titanium planes and one aluminum plane leading to a crystallographic sequence of six planes in the unit cell, which can be written

$$AB'ABA'B, \tag{1}$$

where the primes denote the aluminum planes. The metalloid atoms in the H phase are located in the octahedral cavities between the Ti planes. Thus ascribing Greek letters for C or N planes one can characterize the structure by the sequence

$$\gamma AB'A \gamma BA'B. \tag{2}$$

It must be emphasized that the Ti-Al-Ti stacking is clearly a close packing of a fcc or hcp metal. The choice of the $2c$ Wyckoff position for the aluminum atoms leads to the sequence
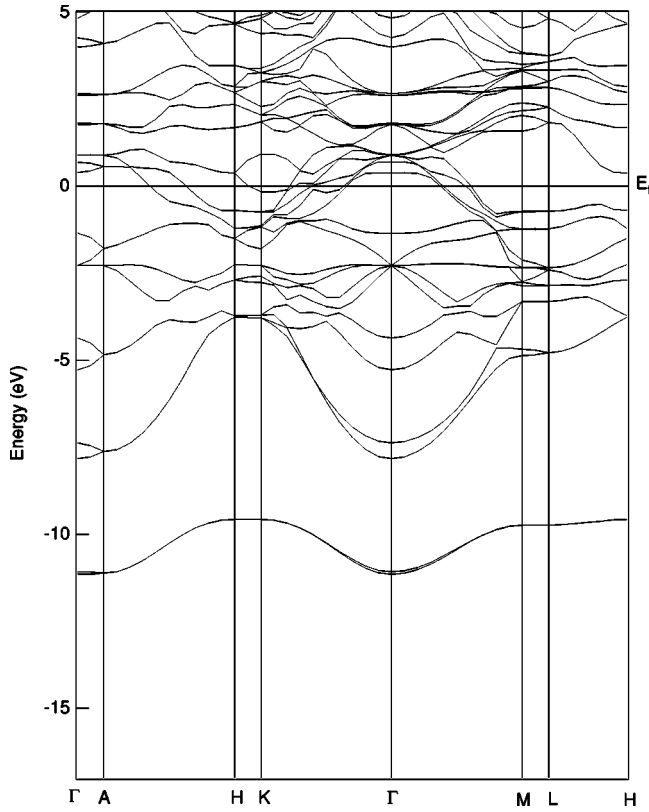
$$\gamma AA'A \gamma BB'B, \tag{3}$$

which includes an AA stacking sequence [cf. Figs. 1(a) and 1(b) in Ref. 1] usually considered as energetically prohibitive in metals.

Consequently the total energy resulting for such crystal structure is expected to be high or prohibitive. In order to check the consequence of the choice of the stacking of metallic planes we have performed calculations for the both structures of Ti$_2$AlC and Ti$_2$AlN. In the following, the two crystallographic structures are refered by their corresponding formula numbers (2) and (3) hereabove. We calculate the electronic structure in the framework of a full-potential lin-

earized plane-wave method (FLAPW). The influence of the exchange and correlation potential has been tested using the generalized gradient approximation[8] (GGA) correction or the local spin density using the WIEN code.[9] In this method no approximation on the shape of the potential is made. We have used separation radii between valence states and core states of 1.5, 1.8, and 1.5 a.u. for the Ti, Al, and C (or N) atoms, respectively and 500 k points in the Brillouin zone. The semicore states (Al $2p$, Ti $3s$, Ti $3p$) are described as a combination of plane-waves and local orbitals.[10] The total energy was converged to 10^{-4} Ryd. The spheres separate the space between core states treated as atomic orbitals and valence states treated as plane waves in the interstitial space. Unlike the more classical band-structure calculations based on muffin-tin potentials such as linear muffin-tin orbital (LMTO) the spheres must not overlap in FLAPW and the results of the calculation are independent of the sphere radii. We have checked that the results are not dependant on sphere radii by increasing the radii up to 1.8 a.u. that still insures that there is no overlap between Ti and C (or N) spheres. The results have been compared with LMTO in the atomic sphere approximation (ASA) and FLAPW using the local-density approximation (LDA) correction for the exchange and correlation potential. Since the general shapes of the band structures and densities of states (DOS) are similar we present only the graphs for the FLAPW-GGA calculations that are assumed to be more accurate.

II. Ti$_2$AlC

The band structure (BS) and the total density of states (TDOS) of the Ti$_2$AlC phase with structure (2) calculated with the FLAPW-GGA method are presented in in Figs. 1 and 2, respectively. The same calculations under the LAPW LDA were very similar, it is also consistent with the BS previously calculated within a LMTO approach.[11] A minimization of the total energy with respect to the unit-cell volume has been performed. This volume is found to be close to the experimental one[12,13] with a deviation of less than 1%, even though the c/a ratio and the z coordinate of titanium atoms, which are free parameters in the space group, should in principle be relaxed. The BS shows a first deep band with low dispersion (width: 1.55 eV), which is mainly due to C s and Ti sp states as can be seen on the projected densities of states (PDOS) [Fig. 3(a)]. A fairly

FIG. 1. LAPW-GGA band structure for Ti_2AlC.

FIG. 3. Projected densities of states for Ti_2AlC: the C s-Ti p hybridization (a), and the C p-Ti d and Ti d-Al p hybridizations (b) are shown. The relative intensities of the PDOS are not significant in this figure.

large indirect gap (1.75 eV) between the points Γ and K of the Brillouin zone separates these states from a series of bands containing C p, Ti d, and Al p states. However the main hybridization in this energy window concerns Ti d and C p states [Fig. 3(b)]. A second smaller gap is also present but it results only in a pseudogap in the TDOS. The indirect gap between points K and M is slightly negative and thus appears only as a minimum in the TDOS at -2.2 eV. From -2 eV and up to the Fermi level one finds mainly hybridized Ti d and Al p states [Fig. 3(b)]. This band structure bears some resemblance with the one presented by Zhou and Sun in that the Ti-C interaction is not strongly affected by the stacking sequence of the metallic atoms. The same calculation of the BS has also been done for the structure (3). The
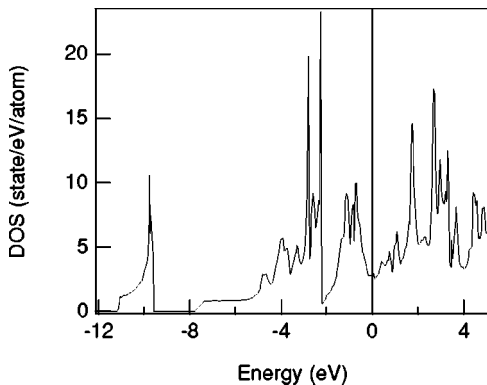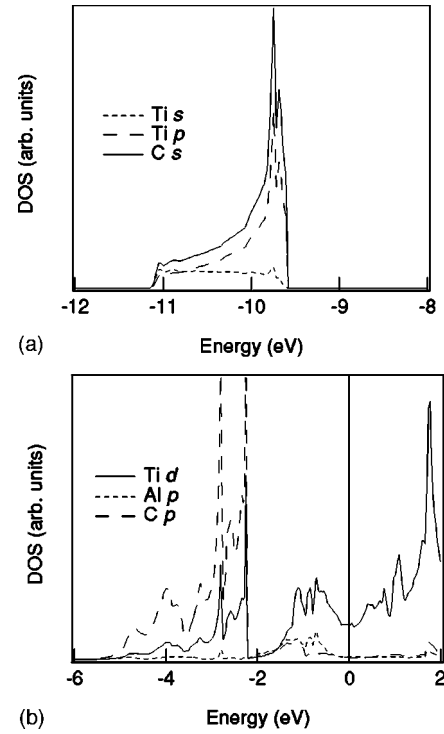
total energy of the structures (2) and (3) are reported in Table I for LMTO ASA, FLAPW LDA, and FLAPW GGA approaches, respectively. The total energy of the structure (3) used by Zhou and Sun was always found to be unfavorable whatever the theory used. In the case of the GGA correction the excess of energy is 0.46 Ry that represents an important difference. We found that the TDOS is very similar for the two crystallographic structures up to -2 eV. Figure 4 shows a comparison of the TDOS in the $[-2,2]$ eV range. In this region one can see that the Ti d-Al p hybridization is different for structure (3). A peak at -0.1 eV that has been found to be due to Ti d and Al d states, is likely to influence strongly the magnitude of the TDOS at Fermi level. Since the Ti-C bonds are mainly located at low energies, the screening of the titanium atoms is probably efficient enough for the carbon not to be affected by the position of aluminum atoms. This is the reason why the band structure of Zhou and Sun[1] and Fig. 1 of the present work exhibits similar features in deep levels, which depend principally on the C-Ti interaction, but not in the vicinity of the Fermi level.

TABLE I. Total energies of H phases. The structures refer to the formulae numbers in the text.

Composition	Structure	LMTO ASA (Ryd)	FLAPW LDA (Ryd)	FLAPW GGA (Ryd)
Ti_2AlC	Eq. (2)	-7939.1827	-7935.4175	-7954.7373
Ti_2AlC	Eq. (3)	-7939.0629	-7934.9981	-7954.2731
Ti_2AlN	Eq. (2)	-8005.8063	-8002.0672	-8021.6281
Ti_2AlN	Eq. (3)	-8005.7144	-8001.6582	-8021.1971

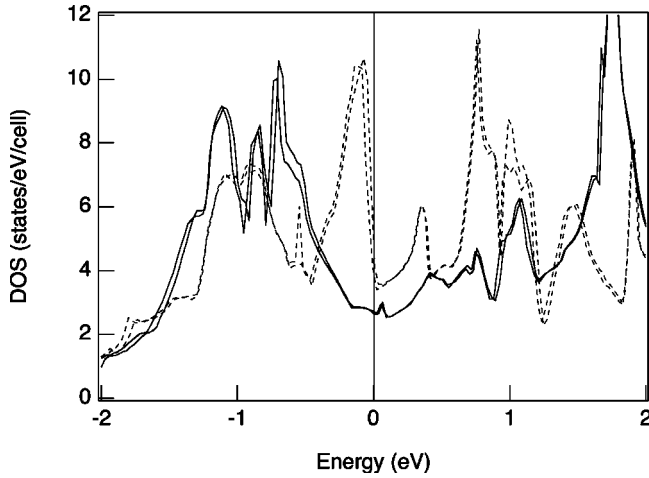FIG. 2. Total DOS for Ti_2AlC calculated with LAPW GGA.

FIG. 4. TDOS for the structures (2) (full lines) and (3) (dashed lines) in Ti_2AlC. In each case two lines are displayed corresponding to GGA or LDA corrections.

Notice also that the Fermi level is located in a region of minimum density of states (2.67 states/eV/cell, Table II). The states at Fermi level are mainly Ti d and Al p. Carbon does not contribute significantly to the DOS at the Fermi level and therefore is not involved in the conduction properties. We note that Ti d electrons are mainly contributing to the DOS at Fermi level and should be involved in the conduction properties although d electrons are generally considered as low efficient conductors. Al electrons do not contribute significantly at Fermi level due to a scooping effect resulting from the presence of the titanium d states. Furthermore, the plot of the band structure shows dispersed bands along the HK direction (Fig. 1). Because s and d electrons may have different conduction properties, it would be difficult in the present state of analysis to assess that the H phase would have anisotropic conduction properties as stated in the paper of Zhou and Sun.[1] This point requires a more detailed study.

III. Ti_2AlN

In the case of Ti_2AlN the experimental volume has been used. The BS and the TDOS for the correct Ti_2AlN phase are presented in Figs. 5 and 6, respectively. The main difference with the previous case is that the electrostatic attraction of nitrogen is higher than that of carbon. Thus the bands associated with nitrogen are lower in energy and narrower. The N s-Ti p band located below -15 eV is only 1 eV in width [Fig. 7(a)]. The energy gap between N s-Ti p and N p-Ti d

TABLE II. Magnitude of TDOS at Fermi level.

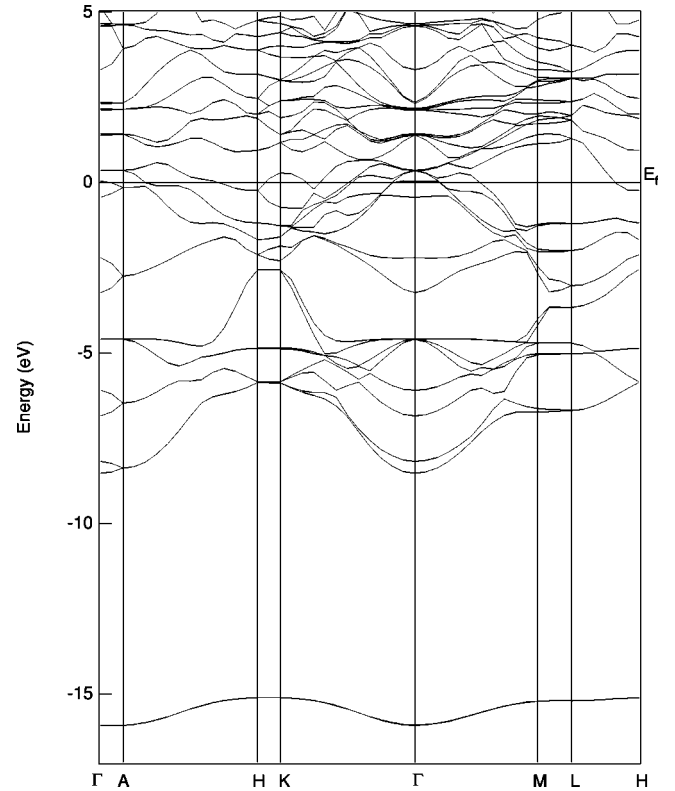| Composition (Structure)	LMTO ASA (states/eV/cell)	FLAPW-LDA (states/eV/cell)	FLAPW-GGA (states/eV/cell)
Ti_2AlC [Eq. (2)]	3.28	2.63	2.67
Ti_2AlC [Eq. (3)]	7.75	4.07	4.01
Ti_2AlN [Eq. (2)]	3.03	3.81	3.84
Ti_2AlN [Eq. (3)]	6.35	4.72	4.86

FIG. 5. LAPW-GGA band structure for Ti_2AlN.

states is equal to 6.67 eV and much larger than in the C s-Ti p and C p-Ti d case. Thus the Ti d states are also globally shifted to lower energy. The N p-Ti d band is also more separated from the Al p-Ti d band [Fig. 7(b)] than the corresponding C p-Ti d band in the previous case. A minimum in the TDOS appears between -4.6 eV and -2.2 eV. Contrary to Zhou and Sun[1] we find that the replacement of C by N does not result in a decrease but in an increase of the TDOS at the Fermi level that is then equal to 3.84 states/eV/cell. This is a consequence of the fact that the Ti d states have been pushed down by the more attractive nitrogen atom. It is therefore expected that the electric conductivity of Ti_2AlN should be greater than that of Ti_2AlC, in agreement with the experimental results.[12,13] The Al p states are also slightly pushed down to lower energy. It can be
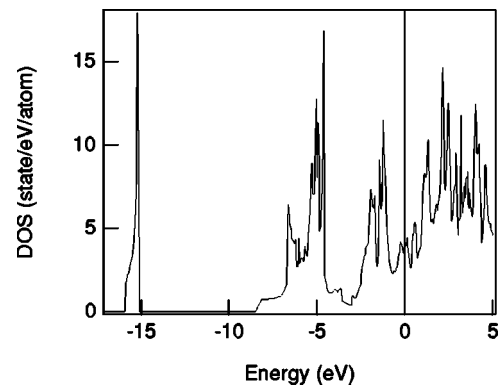

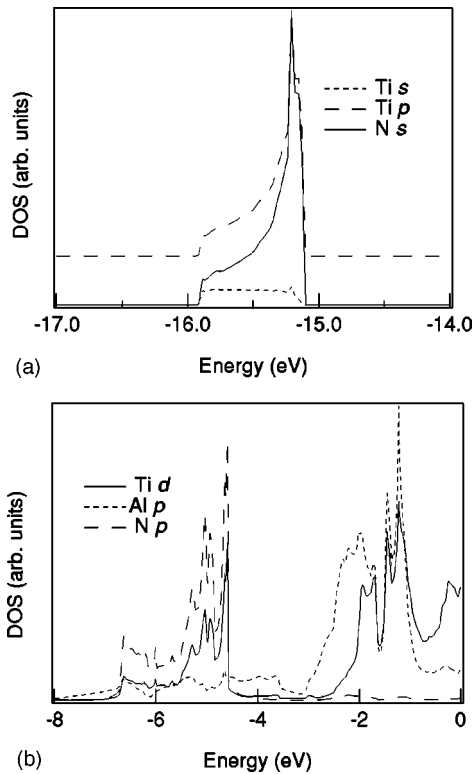FIG. 6. Total DOS for Ti_2AlN calculated with LAPW GGA.

FIG. 7. Projected densities of states for Ti_2AlN: the N s-Ti p hybridization (a), and the N p-Ti d and Ti d-Al p hybridizations (b) are shown. A shift of the Ti p DOS has been done in (a) for better clarity. The relative intensities of the PDOS are not significant in this figure.

concluded that the Ti d-Al p bonds are stronger in Ti_2AlN than in Ti_2AlC.

As in the case of the carbide, all the calculation of the BS of the nitride Ti_2AlN with structure (3) leads to a total energy that is less favorable than the one of structure (2). The excess of energy is 0.43 Ryd (Table I) in the case of the FLAPW-GGA calculation. The comparison of the TDOS for both structures exhibit the same differences than in the previous case. The spurious peak due to Ti d and Al d states in structure (3) is now located at -0.5 eV (Fig. 8).
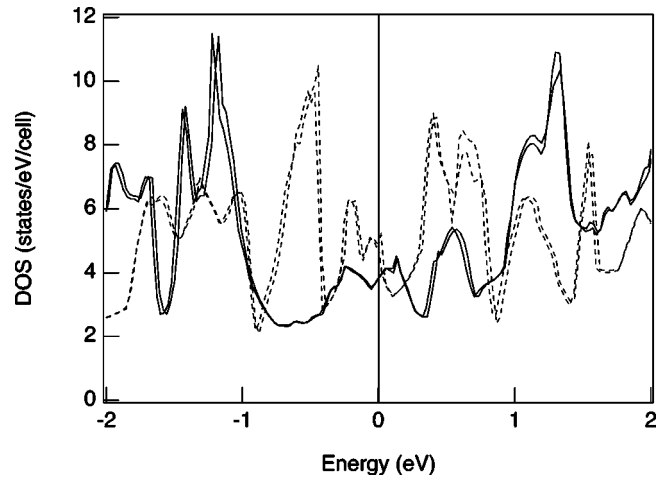

FIG. 8. TDOS for the structures (2) (full lines) and (3) (dashed lines) in Ti_2AlN. In each case two lines are displayed corresponding to GGA or LDA corrections.

IV. CONCLUSIONS

FLAPW calculations for the two crystallographic structures (2) and (3) under consideration show that the total energy is always higher for structure (3). This energy difference is to be attributed to the "AA" metallic stacking in structure (3). Although deep states involving Ti-C or Ti-N bond are similar in both structure, the features related to Al-Ti bonds close to Fermi level are not. The crystal structure (3) results in a peak in the TDOS due to Ti d-Al p states (Figs. 4 and 8) just below Fermi level in the case of Ti_2AlC that sensitively affects the TDOS at Fermi level. FLAPW calculations predict also that the electric conductivity of the H phase should be higher in Ti_2AlN than in Ti_2AlC in agreement with previous experimental results.[12,13]

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