

Electronic structure and chemical bonding of α - and β - Ta_4AlC_3 phases: Full-potential calculation

Wei Lu^{a)}

Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, People's Republic of China

Xiaohui Deng

Department of Physics, Hengyang Normal University, Hengyang 421008, People's Republic of China

Hai Wang and Haitao Huang

Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, People's Republic of China

Lianlong He

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China

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First-principles total-energy and heat of formation calculations on α and β polymorphs of Ta_4AlC_3 have been made with a full-potential electronic structure program with the generalized gradient approximation, which shows that α phase is more stable than β phase. The charge transfer and chemical bonding of the two phases were investigated quantitatively by using Bader's quantum theory of atoms in molecules (AIM). The results show that the bonding between Ta1-C2 is stronger in α phase than β phase, which leads to the stability of α phase.

I. INTRODUCTION

The layered ternary $\text{M}_{n+1}\text{AX}_n$ (MAX) compounds, where $n = 1-3$, M is an early transition metal, A is an A-group element, and X is C or N, have been studied extensively in recent years.¹⁻⁶ These materials exhibit an unusual combination of mechanical, electrical, and thermal properties.⁷⁻¹⁰ For M_2AX (211), many compounds have been characterized, such as Ti_2AlC , Ti_2AlN , etc. For M_3AX_2 (312), some of the compounds were identified, i.e., Ti_3AlC_2 , Ti_3SiC_2 . For M_4AX_3 (413), only a few compounds were reported until now. The earliest $n = 3$ ternary reported by Barsoum et al. was Ti_4AlN_3 with a hexagonal unit cell, space group $P6_3/mmc$.^{11,12}

Recently, Palmquist et al.¹³ first reported on another 413 phase in Ta-Al-C system, Ta_4AlC_3 . Then Manoun et al.¹⁴ confirmed the existence of this phase and studied the stability under high pressure. The space group and lattice constant of this phase were also reported. Etzkorn et al.¹⁵ successfully synthesized the single crystal of Ta_4AlC_3 phase. The lattice constant ($a = 0.31123$ nm, $c = 2.4111$ nm) and atomic positions were also obtained in their work. The lattice constants they obtained have a

considerable deviation with that of Manoun et al. who reported ($a = 0.3087$ nm, $c = 2.370$ nm). A closest packing of metal atoms with a sequence ABABCBBCBC along the c axis, which is the same as Ti_4AlN_3 , were reported. Lin et al.^{16,17} used a combined technique of x-ray diffraction (XRD), convergence beam electron diffraction, high-resolution electron microscopy (HREM), and Z-contrast imaging to characterize the crystal structure of Ta_4AlC_3 . They found a different crystal structure from Ti_4AlN_3 . A closest packing of metal atoms with a sequence ABABABABAB along the c axis were obtained. The lattice constants they refined ($a = 0.3091$ nm, $c = 2.3708$ nm) are similar with that obtained by Manoun et al.¹⁴ Recently, Eklund et al.¹⁸ also synthesized and characterized the Ta_4AlC_3 phase by Rietveld refinement of synchrotron XRD. Their result shows that Ta_4AlC_3 belongs to $P6_3/mmc$ space group with a and c lattice parameters of 0.310884 and 2.40776 nm, respectively, which is similar with that reported by Etzkorn et al.¹⁵ Therefore, they suggested that two Ta_4AlC_3 phases exist with the same space group, but different atomic position in a unit cell. The Ta_4AlC_3 , with atomic position the same as Ti_4AlN_3 , was named as α phase and another one is β phase. [The unit cells of the two polymorphs are schematically shown in Figs. 1(a) and 1(b)]. However, the stability of those two phases has not been studied until now.

^{a)}Address all correspondence to this author.

e-mail: imrwlu@gmail.com
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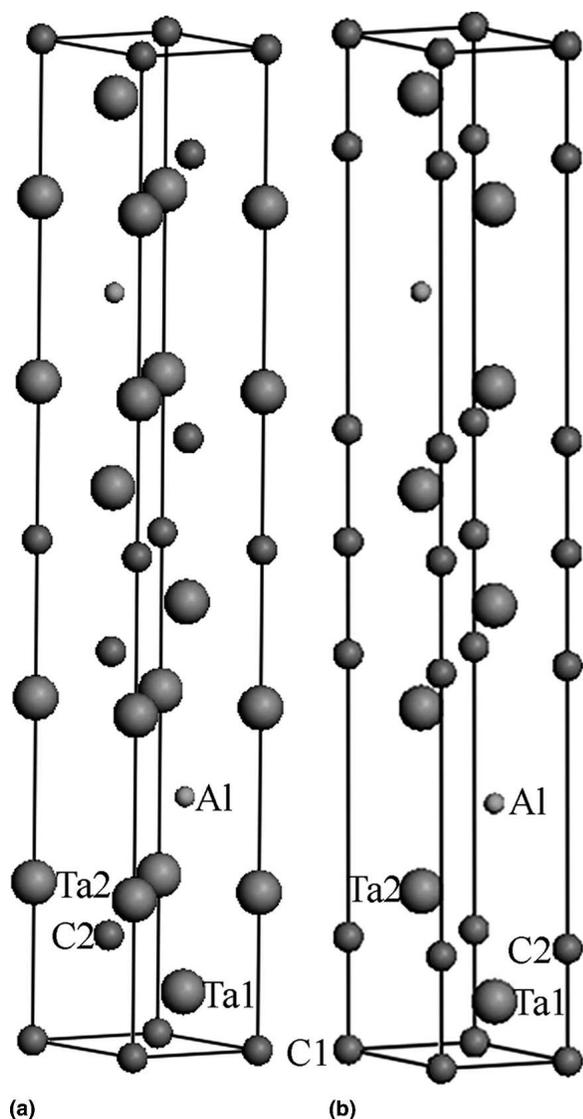


FIG. 1. Structure models of Ta_4AlC_3 (a) α and (b) β polymorphs, respectively.

In the present work, the stability of α and β phases will be studied by first principle. The different atomic configurations of α and β phases are expected to affect their bonding properties. To obtain a clear bonding character in the two polymorphs, we carried out an analysis of the electronic density using the Bader's atoms in molecules (AIM) methods.^{19–21}

II. THEORETICAL DETAILS

The calculations presented in this work were performed by using the WIEN2k package, which is an implementation of the full-potential linearized augmented plane wave (FLAPW) plus local orbitals (lo) method within the framework of the density-functional theory.^{22–24} In the present study, the Perdew-Burke-

Ernzerhof generalized gradient approximation (GGA) for the exchange correlation potentials was used.²⁵ Relativistic effects were taken into account within the scalar-relativistic approximation. The total and partial densities of states (DOS) were obtained using a modified tetrahedron method of Blöchl et al.²⁶ The atomic sphere radii 2.0, 1.9, and 1.7 a.u., were used for Ta, Al, and C, respectively, in the full calculation. To achieve a satisfactory convergence, the basis function was expanded up to $R_{\text{MT}}K_{\text{Max}} = 8$, where R_{MT} is the smallest of all atomic sphere radii and K_{Max} is the plane wave cutoff. The k -point sampling in the total Brillouin zone was conducted with $20 \times 20 \times 2$ mesh, which represents 88 k -points in its irreducible part. The self-consistent iteration was carried out with a total energy convergence tolerance of less than 0.1 mRy.

The structure optimization for α - and β - Ta_4AlC_3 came from previous reports.^{14–18,27} The whole relaxation process, as indicated in previous work,²⁸ includes four steps: (i) relaxing the atomic coordinates with fixed lattice parameters; (ii) optimizing the volume with the fixed c/a ratio, and the atomic coordinates obtained in the previous step; (iii) optimizing c/a ratio with the fixed theoretical volume and atomic coordinates; and (iv) the atomic coordinates were relaxed again with the fixed theoretical lattice parameters.

The theory of AIM is an interpretative theory that aims to recover chemical insight from modern high-resolution electron densities.^{19–21,29} It provides a rigorous definition for the chemical bonds linked with atoms in molecules/solids, and thus one can go beyond a qualitative description of the strength of interatomic interaction.³⁰ The essence of molecular structure is contained in the scalar field of the charge density, $\rho(\mathbf{r})$ defined over three-dimensional space. The topology of $\rho(\mathbf{r})$ gives the definition of molecular structure in terms of its critical point (CP), where the gradient of $\rho(\mathbf{r})$ vanishes. There are four kinds of CPs: a local maximum, a local minimum, and two kinds of saddle points. These critical points are denoted by the rank and signature of the Hessian matrix $[\nabla^2\rho(\mathbf{r})]$ of the electron density. The rank is the number of nonzero curvatures of Hessian matrix and the signature is the number of positive curvatures minus the number of negative curvatures. For energetically stable molecules or crystals, the rank is three. There are just four possible signature values corresponding to four kinds of CPs as referred to before. That is, CP (3, -3) corresponds to local maxima (nucleus or non-nuclear attractors³¹). CP (3, -1) is called a bond critical point, which corresponds to the saddle point. CP (3, 1) is called a ring critical point, which also corresponds to the saddle point. CP (3, 3) is called a cage critical point, which corresponds to a local minimum. The curvatures are denoted as h_i ($i = 1-3$) in an increasing order. Thus, a bond CP should have $h_1 \leq h_2 < 0 < h_3$.^{21,32,33}

TABLE I. Experimental and calculated lattice parameters, atomic positions (fractional coordinate) of Ta₄AlC₃ phase. For both α and β phase, Al and C1 refer to the Al atom occupy $2c$ Wyckoff position and C atom occupy $2a$ position.

	a (nm)	c (nm)	c/a	Ta1	Ta2	C2	B (GPa)
α	0.3112 ^{a,b}	2.4111	7.75	(1/3, 2/3, 0.05820)	(0, 0, 0.15801)	(2/3, 1/3, 0.1079)	262.2
	0.3109 ^{a,c}	2.4078	7.74	(1/3, 2/3, 0.05453)	(0, 0, 0.15808)	(2/3, 1/3, 0.1032)	
	0.3139 ^{b,d}	2.4209	7.71	(1/3, 2/3, 0.05531)	(0, 0, 0.15783)	(2/3, 1/3, 0.1083)	
β	0.3087 ^{a,e}	2.370	7.68				259 ^f
	0.3091 ^{a,f}	2.3708	7.67				
	0.30699 ^{b,f}	2.4198	7.88	(1/3, 2/3, 0.05524)	(2/3, 1/3, 0.16016)	(0, 0, 0.11125)	
	0.3103 ^{b,d}	2.4635	7.94	(1/3, 2/3, 0.05496)	(2/3, 1/3, 0.15989)	(0, 0, 0.1108)	

^aExperimental result.^bTheoretical result.^cRef. 15.^dRef. 18.^ePresent work.^fRef. 14.^gRef. 16 and 17.^hRef. 27.

In the AIM theory, a basin is associated to each attractor (3, -3) critical point. The boundary condition demands that the flux in the gradient vector field of the charge density $\rho(\mathbf{r})$ vanish at every point of the surface $S(Q, \mathbf{r})$, which bounds an open system Q . Therefore, the surface is one of zero flux in $\nabla\rho$:

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad ,$$

where $\mathbf{n}(\mathbf{r})$ is the normal to the surface at point \mathbf{r} . This definition is equally applicable to a free atom, for which the atomic surface lies at infinity, an atom in a molecule and an atom in a solid. The charge of an atom is defined as the charge contained within its atomic surface.

III. RESULTS AND DISCUSSION

A. Structure and stability

The lattice constants and bulk modulus that are determined by least squares fit of the E - V curves (total energy versus volume) calculated by the density function theory (DFT) to Murnaghan's equation of state³⁴ are summarized in Table I. It can be seen that the calculated lattice constants in the present work agree well with the experimental result for α phase. However, the calculated lattice constant of β phase is slightly larger in the c direction compared with experimental results. According to a previous investigation of $M_{n+1}AX_n$,^{28,35,36} it is concluded that the theoretical lattice constant in c direction of β phase is always larger than α phase because of the variation of bonding strength in the unit cell. According to a previous report,³² it is shown that the weakness of bonding between Ti-Si leads to the increase of c/a ratio for β -Ti₃SiC₂ phase. According to our quantitative analysis in Sec. III. B. 3, it will be shown that the weaker bonding between Ta1-C2 for β -Ta₄AlC₃ phase leads to the in-

crease of c axis. Therefore, it is reasonable in theory that the ratio of β phase is larger than that of α phase. The bulk modulus of these two phases reported in previous work,^{13,27} showed a B value of close to 261 GPa, matching well with the present results.

The theoretical heat of formation of Ta₄AlC₃, which is composed of Ta, Al, and C, can be obtained using the following equation:

$$\Delta H = E(\text{Ta}_4\text{AlC}_3) - [4E(\text{Ta}) + E(\text{Al}) + 3E(\text{C})] \quad . \quad (1)$$

E stands for the total energy obtained from the WIEN2k code for unit cells of Ta₄AlC₃, Ta (space group: $Im\bar{3}m$, 1 atom/unit cell), Al (space group: $Fm\bar{3}m$, 1 atom/unit cell) and graphite (space group: $P6_3/mmc$, 4 atoms/unit cell), respectively. To achieve a satisfactory convergence, 5000 k-points were sampled in the total Brillouin zone for metals and graphite. To precise the total energy, all of the elemental crystals were also fully relaxed. The total energy of the two Ta₄AlC₃ phases and corresponding elemental crystals are listed in Table II. The heats of formation of α and β phase are -73.8 kJ/mol and -66.1 kJ/mol, respectively, which means that α phase is more stable than β phase.

TABLE II. Calculated lattice parameters and corresponding total energy of α , β phase, and the elemental structure and heats of formation of α and β phase.

	a (nm)	c (nm)	E (Ry)	ΔH (kJ/mol)
α	0.313916	2.420897	-251447.070488	-73.8
β	0.310344	2.463548	-251446.985645	-66.1
Ta	0.331741		-31252.206037	
Al	0.403994		-485.644160	
C	0.246240	0.687473	-304.829009	

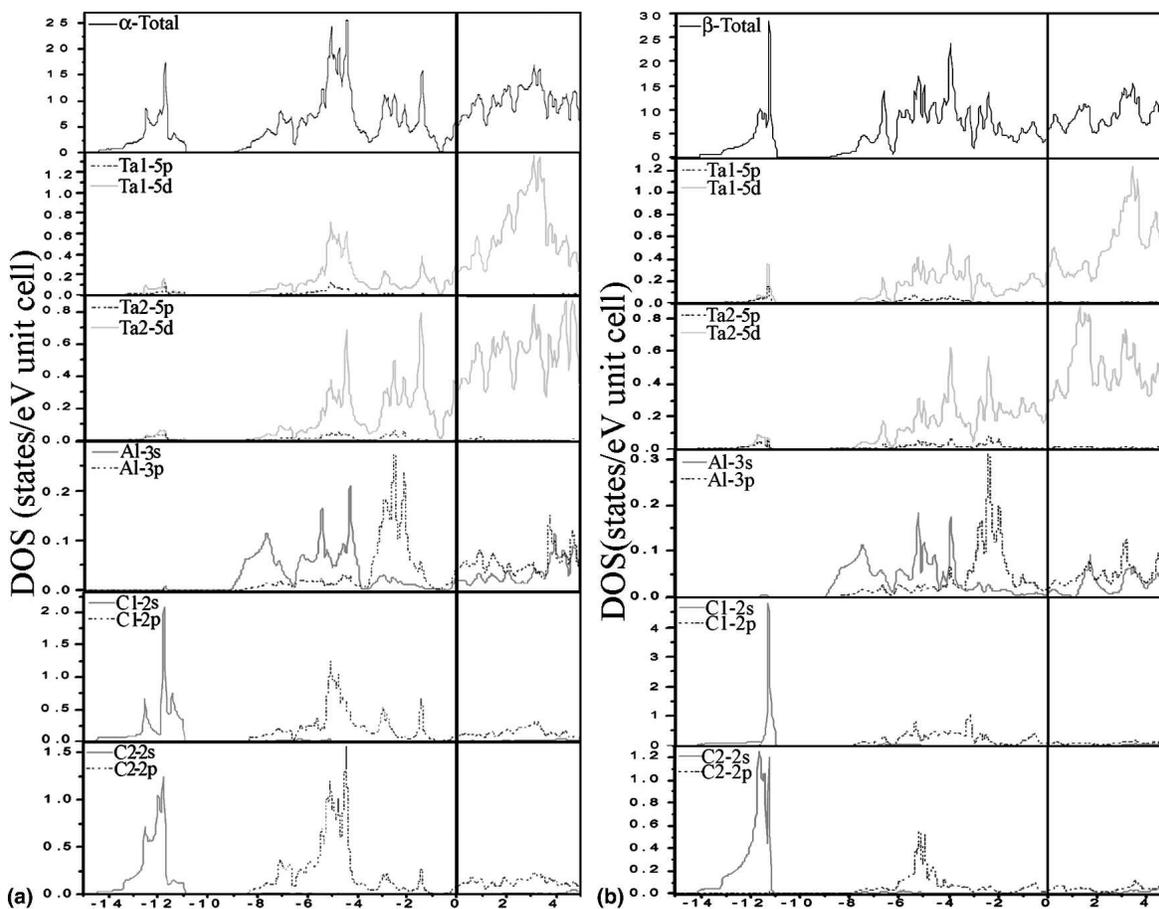


FIG. 2. Total and partial DOS curves of (a) α phase and (b) β phase. The Fermi level is set to 0 eV and indicated by a vertical solid line.

B. Electronic properties

1. Density of states

The calculated total DOS and partial DOS for α and β phases are shown in Figs. 2(a) and 2(b), respectively. It can be seen that total DOS both for α and β phase can be mainly divided into three bands. From -15 eV to -10 eV, the peak mainly comes from the $2s$ states of C1 and C2. The d states of Ta1 and Ta2 also have some minor contribution to this peak. The conduction band originates predominantly from Ta1 and Ta2 $5d$ states. All of these elements have contribution to the valence band. It can be seen that Ta $5d$ states and C $3p$ states have an equal width and similar peak shapes (from -8 eV to -3 eV), which indicates obvious hybridizations between Ta and corresponding C atoms. The Al $3s$ and $3p$ states together have an equal valence bandwidth and peak shapes as Ta $5d$ states (from -8 eV to Fermi level), which also means that Al has hybridization with the nearest Ta2 atom. The main contribution to the total DOS at the Fermi level $N_{\text{tot}}(E_{\text{F}})$ in all α and β phases originates from the Ta $5d$ states. The $N_{\text{tot}}(E_{\text{F}})$ for α and β phases are 5.24 and 4.11 states/eV per unit cell, respectively, which indicate the conductivity of α phase is higher than β phase.

2. Charge density

To illustrate the bonding picture in α and β phases, the valence charge density and the difference charge density maps of $(11\bar{2}0)$ plane were plotted in Figs. 3(a)–3(d). By comparing analysis Figs. 3(a) and 3(c), it is shown that some charge densities are surrounding Ta1, C1, C2 atoms and Ta2, C2 atoms, which indicates that the bonding between Ta1 with C1, C2 and Ta2 with C2. In α phase, the atoms of C1, Ta1, C2, and Ta2 form a chain bonding structure. The distribution of charge density around the layer of Al is uniform in both α and β phase and the gradient of charge density is also smaller than Ta–C layer, which means that Al exhibits more metallic. According to the difference charge density in Figs. 3(b) and 3(d), it can be seen that the gradient of density is increased along Ta–C direction because of the existence of covalent bonding between Ta and C. It also can be seen that there are many dashed line around Ta and solid line around C atoms, which means the charge transfers from Ta to C. Though some charge accumulation near the Al atom as shown in the difference charge density map, it is hard to reveal a bonding character between Al and other atoms from the difference charge density map. So

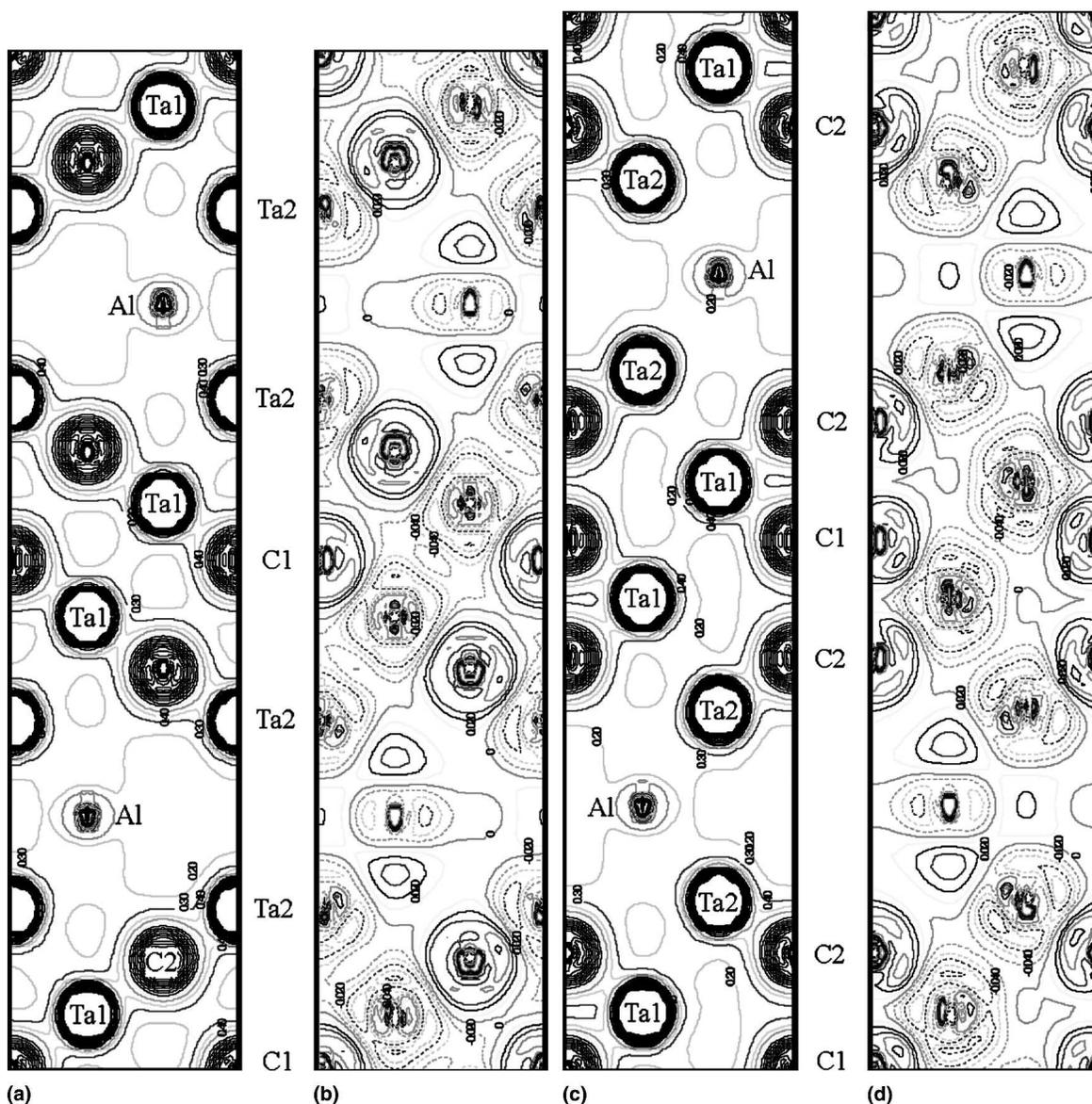


FIG. 3. Valence and difference charge densities ($\text{e}\text{\AA}^{-3}$) in the $(11\bar{2}0)$ plane for (a, b) α phase and (c, d) β phase. (The dashed and solid lines represent negative and positive values in difference charge densities, respectively).

quantitative analysis of bonding character based on the AIM theory will be carried out in next part.

3. Topological analysis and bond critical points

Table III contains the atomic charges within the atomic basins of Ta1, Ta2, Al, C1, and C2 defined as the integrated densities inside the atomic basin. It can be seen clearly that C2 has a larger negative value compared with C1. From the atomic configuration in $(11\bar{2}0)$ plane, it can be seen that C2 is always connecting with Ta1 and Ta2 atoms in both α and β phase. Therefore the charge accumulation in C2 atomic basin is larger than that in C1 atomic basin. Similarly, Ta1 atom always bond with C1 and C2 atoms in both two phases, the charge transfer in

TABLE III. Atomic charges with the corresponding atomic basin for α - and β - Ta_4AlC_3 phase.

	Ta1	Ta2	Al	C1	C2
α	1.875	1.004	-0.097	-1.853	-1.901
β	1.763	1.016	-0.054	-1.811	-1.842

Ta1 atomic basin is larger than that in Ta2 atomic basin. Although, there are some charges that transfer from Al atom as indicated by the dashed line around Al atom in the difference charge density map. However, there are also some accumulations of charge near Al atom along and perpendicular c axis, so its atomic charge in the atomic basin is a small negative value.

TABLE IV. Bonding atoms, bond length, charge density, curvatures, and Laplacian at the bond critical points in both α and β phase.

	Bond	l(Å)	ρ (eÅ ⁻³)	h_1 (eÅ ⁻⁵)	h_2 (eÅ ⁻⁵)	h_3 (eÅ ⁻⁵)	$\nabla^2\rho$ (eÅ ⁻⁵)
α	Ta1-C1	2.25	0.5513	-1.79057	-1.78985	7.57681	3.996
	Ta1-C2	2.22	0.5708	-1.71827	-1.68213	8.09495	4.695
	Ta2-Al	2.95	0.2512	-0.29690	-0.18556	0.62634	0.144
β	Ta2-C2	2.17	0.6462	-2.20894	-2.17182	8.68297	4.304
	Ta1-C1	2.25	0.5741	-2.03181	-1.95276	7.55271	3.569
	Ta1-C2	2.26	0.5492	-1.87468	-1.74069	7.42017	3.805
	Ta2-Al	2.94	0.2619	-0.30702	-0.19448	0.58031	0.079
	Ta2-C2	2.16	0.6653	-2.41233	-2.33546	8.84202	4.094
	C1-C2	2.73	0.2809	-0.01301	-0.01301	2.08868	2.062

The calculated nonequivalent bond CPs for α and β phases, shown as the bonding atoms, are listed in Table IV. The bond length, charge density, curvatures of Hessian matrix of the electron density, and Laplacian are also given in Table IV. From this table, it can be seen that the bond critical point between Ta2 and Al atoms exists in both α and β phase, which means the existing of bonding between Ta2 and Al atom is in both phases. From the list of bonding atoms, it can be seen that there is also the C1 and C2 bond in β phase. The bond length is 2.73 Å. It is obviously longer than the bond length of C atoms in a same layer in graphite and C atoms in diamond. Therefore the bond strength between C1 and C2 in β phase is not strong. By comparing the analysis of bond critical points in α and β phases, it can be seen that the charge density between Ta1 and C2 in α phase is obviously larger than that in β phase. The larger accumulation of charge density between Ta1 and C2 lead to a strong bond length in α phase, which will stabilize the α phase. It is the main reason that the heat of formation of α phase is more negative than β phase. The weaker bond length of Ta1 and C2 in β phase will also lead to the increase of lattice constant along the c axis.

In the topology theory,^{21,32,33} for a given bond CP, the ratio of principal curvatures $|h_1|/h_3$ together with the Laplacian provide information for a classification of chemical bonding. A small value $|h_1|/h_3 \ll 1$ is typical for closed-shell (ionic, hydrogen, and Van der Waals) interactions, while for covalent bonding this ratio increases with bond strength. Accordingly, the Laplacian is positive and large for ionic bonding, but small or negative for covalent bonds. According to a previous definition, it can be seen that all of the bond critical points in α and β phases do not absolutely belong to covalent bonds. The interaction between C1 and C2 in β phase is close to Van der Waals bonding. According to the curvatures and Laplacian, it is seen that the interaction between Ta2 and Al is close to covalent bond compared with other bond in Ta₄AlC₃ phases. However, the charge accumulation between Ta2 and Al atoms is small, so the bond strength between those two atoms is weak in both α and β phase. As suggested in previous work,³² the

constraints of the atoms received in crystals must be taken into account when the AIM theory is applied to solid-state phases.

IV. CONCLUSIONS

In summary, we studied the structure stability, electronic structure, and chemical bonding of the hexagonal α - and β -Ta₄AlC₃ compounds using the all-electron and full potential first principles method. The results indicate that α phase is more stable than β phase because the heat of formation of α phase is more negative than that of β phase. The conductivity of α phase is higher than β phase. The topologist analysis showed that C2 gets more charges than C1 atoms, meanwhile Ta1 transfer more charges than Ta2 atoms. The bonding strength between Ta1 and C2 is significantly stronger in α phase than in β phase, which leads to α phase being more stable than β phase and increases the ratio of c/a of β phase. There are bonding effects between Ta2 and Al atoms in both α and β phase. Only a weaker C1-C2 bond was formed in β phase.

V. ADDITIONAL NOTE

During the review of this manuscript, a contribution on the first principle calculation of α - and β -Ta₄AlC₃ polymorphs was published,³⁷ which also confirmed that α phase is more stable than β phase and the ratio of c/a of β phase is increased.

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