Band filling and structural stability of cubic trialuminides: YAl_3, $ZrAl_3$, and $NbAl_3$

Jian-hua Xu
Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 200 050, China

A. J. Freeman
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208
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The electronic structure and the structural stability of the trialuminides YAl_3, $ZrAl_3$, and $NbAl_3$ in the cubic $L1_2$ and tetragonal $D0_{22}$ structures were investigated by means of the total-energy all-electron self-consistent linear muffin-tin orbitals (LMTO) method. The variation of the stability across the constituent transition-metal series can be understood simply in terms of the band filling of the bonding states. And surprisingly, the simple rigid-band approximation appears adequate to describe the structural stability of these (*p-d* covalent) trialuminides.

The study of the correlation between the electronic structure and the crystal structure of the transition-metal (TM) trialuminides has twofold significance. First, for developing super-aluminum-based alloys for elevated temperature applications, Fine *et al.*[1] have found low-mismatch (therefore, low interfacial energy) coherent coplanar $L1_2$ structured precipitates [for instance, $Al_3(Zr_{0.25}V_{0.75})$], which can retard the coarsening rate significantly in the Al-based alloys. However, the mismatch between the precipitates and the aluminum matrix depends strongly upon the crystal structure of the precipitates. Secondly, from the experimental observations it has been known that the stable structures of the TM trialuminides always adopt four different structures—the cubic $L1_2$, the tetragonal $D0_{22}$ or $D0_{23}$, and the hexagonal $D0_{19}$—which vary regularly with the constituent TM atoms. For example, YAl_3 (Ref. 2) has hexagonal $D0_{19}$-type structure at low temperature and rhombohedral $BaPb_3$-type structure at high temperature; a third modification (the $L1_2$ structure) has been observed above 950 °C. In addition, the rhombohedral $BaPb_3$-type structure of YAl_3 can be considered to consist of the purely hexagonal ($D0_{19}$-type) stacking and the purely cubic ($L1_2$-type) stacking. $ZrAl_3$ crystallizes as a secondary phase in the aluminum solid solution in the metastable cubic $L1_2$ structure;[3] after annealing above 510 °C, it transforms into a (stable) tetragonal $D0_{23}$ structure. Finally, $NbAl_3$ has no polymorph; the tetragonal $D0_{22}$ structure is a unique stable structure.[4]

In this paper, we investigate the electronic structures and the structural stability of YAl_3, $ZrAl_3$, and $NbAl_3$ using the local-density total-energy all-electron self-consistent linear muffin-tin orbitals (LMTO) method associated with the atomic-sphere approximation.[5] The calculated total-energy results show that in agreement with experiment the $L1_2$ structure of YAl_3 is energetically favored as compared with the $D0_{22}$ structure; by contrast, for $NbAl_3$ the $D0_{22}$ structure is energetically more stable than the $L1_2$ structure. Furthermore, the variation of the structural stability with the (4*d*) TM constituent can be understood in terms of the band filling of the bonding states.

For these three TM trialuminides we considered the $L1_2$-type and the $D0_{22}$-type structures. Both structures can be viewed as a face-centered derivative lattice; all atoms have the same coordination number (12) and each atom has the same first-nearest-neighbor environment, i.e., there are no TM and TM-atom contacts, and four TM atoms plus eight Al atoms surround each Al. In the calculations, we adopt the experimental lattice constants $a = 6.276$ Å and $c = 4.582$ Å for YAl_3 ($D0_{19}$-type structure),[2] $a = 4.073$ Å for $ZrAl_3$ ($L1_2$-type structure),[3] and $a = 3.845$ Å and $c = 8.6012$ Å for $NbAl_3$ ($D0_{22}$-type structure).[4] We simply assumed that both TM atoms and the Al atom have the same Wigner-Seitz (WS) sphere radii, except that we assumed for YAl_3 that the WS radius of Y (1.77 Å) is larger than that of Al (1.64 Å) because the metallic atomic radius of Y (1.81 Å) is significantly larger than that of Al (1.43 Å). For each aluminide, we calculate the WS radius (r_{WS}) from the experimental lattice constant of its stable structure, and then adopt the same WS radius for the different structures to obtain their lattice constants, which are listed in Table I. For the (hypothetical) $D0_{22}$ structure of the YAl_3 and $ZrAl_3$

TABLE I. The lattice constants of YAl_3, $ZrAl_3$, and $NbAl_3$ (in Å). References a, b, and c are experimental values.

	$L1_2$	$D0_{22}$		$D0_{19}$	
	a	a	c	a	c
YAl_3	4.275	4.123	9.194	6.276	4.582[a]
$ZrAl_3$	4.073[b]	3.928	8.759		
$NbAl_3$	3.991	3.845	8.601[c]		

[a]Reference 2.
[b]Reference 3.
[c]Reference 4.

TABLE II. The total energy ($-E$) (in Ry/f.u.) and the total density of states at E_F [$N(E_F)$] (in states/eV f.u.) of YAl_3, $ZrAl_3$, and $NbAl_3$ in the $L1_2$ and $D0_{22}$ structures, obtained using 18, 60, and 45 k points in the irreducible Brillouin zone for YAl_3, $ZrAl_3$, and $NbAl_3$, respectively.

	YAl_3		$ZrAl_3$		$NbAl_3$	
	$-E$	$D(E_F)$	$-E$	$D(E_F)$	$-E$	$D(E_F)$
$L1_2$	8215.236	1.10	8641.993	1.68	9084.172	2.16
$D0_{22}$	8215.200	2.85	8641.996	1.79	9084.250	0.17

aluminides, we assume the ratio of $c/a=2.23$—chosen from the (approximate) experimental c/a ratio of the $D0_{22}$ TM trialuminides. Note that the discrepancy between the calculated (4.275 Å) and the observed (4.323 Å (Ref. 6) lattice constant for cubic YAl_3 is only about 1%, which is generally considered to be about the error found when the calculated (equilibrium) lattice constant is obtained from the total-energy minimum.

The calculated total energy ($-E$) and the density of states at the Fermi level [$N(E_F)$] for these three trialuminides (YAl_3, $ZrAl_3$, and $NbAl_3$) in the two ($L1_2$ and DO_{22}) structures are listed in Table II. As shown in Table II, the total energy of $L1_2$-structure YAl_3 is about 36 mRy/[formula unit (f.u.)] lower than that in the $D0_{22}$ structure; in contrast, the total energy of $L1_2$-$NbAl_3$ is about 88 mRy/f.u. higher than that in the $D0_{22}$ structure. The total-energy calculation clearly shows that in agreement with experiment $L1_2$-structure YAl_3 is energetically favored as compared with the $D0_{22}$ structure,[7] and the $D0_{22}$ $NbAl_3$ is the stable structure. On the other hand, it is rather difficult to judge the phase stability between these two ($L1_2$ and $D0_{22}$) phases of $ZrAl_3$ due to the closeness of their calculated total energies which is less than 1 mRy per atom (cf. Table II). However, the results still provide a clear trend of increasing (or decreasing) the phase stability of the $D0_{22}$ (or $L1_2$) phase on going from YAl_3 to $NbAl_3$. Moreover, it is interesting to note again that the stable structure is always associated with a lower[8] $N(E_F)$.

To gain insight into the phase stability of the TM aluminides and its variation with the TM constituent at the microscopic level, we investigated the electronic structures of these three trialumindes in the $L1_2$ structure. Figure 1 shows the calculated TM $4d$ and Al $2p$ partial density of states (DOS). It is seen that the covalent interactions are so large that the TM $4d$ and Al $2p$ states almost overlap (or hybridize) completely in the whole energy region from the bottom of the band up to E_F. As seen in Fig. 2, a broad and prominent peak at about -1.5 eV (for YAl_3) and -3 eV (for $ZrAl_3$ and $NbAl_3$) arises from the TM $4d$–Al $2p$ bonding states, and a deep valley, or pseudogap[9] between the bonding states and the nonbonding states located at about 0.5 eV for YAl_3, -0.5 eV for $ZrAl_3$, and -1.0 eV for $NbAl_3$.

According to Friedel's theory of the cohesive energy for TM (Ref. 10) and William's conceptual picture of chemical bonding for ordered TM and nontransition-metal compounds,[11] the essential contribution to the cohesion of the TM compounds is the broadening of the

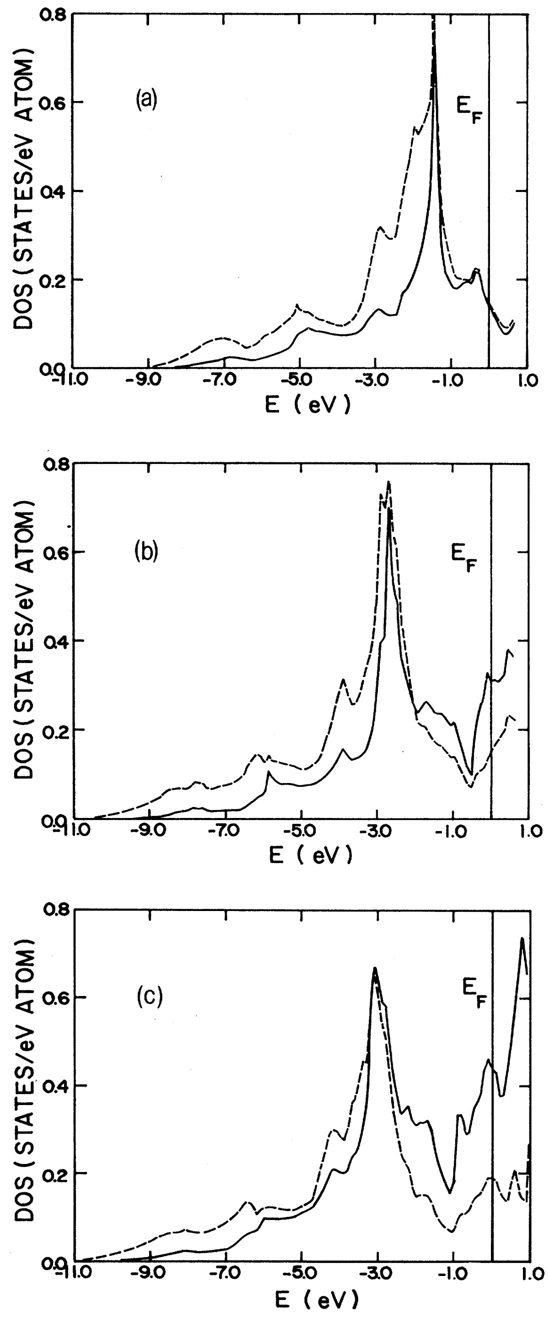

FIG. 1. TM $4d$ and two times the Al $2p$ partial density of states for (a) YAl_3, (b) $ZrAl_3$, and (c) $NbAl_3$: solid line—TM $4d$ states, dashed line—Al $2p$ states.

TM d band and the hybridization between the TM d states and the Al p states; filling bonding or antibonding states will increase or reduce the cohesion (or stability). Similarly, we expect that the phase stability will depend upon the band filling of the bonding states we denote the width of the occupied states by W_{occ} and the width of the bonding states, W_b, as the distance from the bottom of the band to E_F and to the pseudogap, respectively; hence, W_{occ}/W_b can adopted to evaluate the occupied portion of the bonding states, i.e., the band filling of the bonding states.

TABLE III. The width of the occupied states (W_{occ}), of the bonding states (W_b), W_{occ}/W_b, W_{pd}, and the number of valence electrons to be accommodated in the bonding states (n_b) for YAl_3, $ZrAl_3$, and $NbAl_3$ in the cubic $L1_2$ structure (width in eV, n_b in electrons)

	W_{occ}	W_b	W_{occ}/W_b	W_{pd}	n_b
YAl_3	9.34	9.87	0.95	7.87	12.37
$ZrAl_3$	10.71	10.21	1.04	7.82	12.36
$NbAl_3$	11.04	9.93	1.11	7.93	12.28

For these three trialuminides, W_{occ}, W_b, and W_{occ}/W_b are listed in Table III. In addition, the distance from the bottom of the band to the main peak of the (TM $4d$–Al $2p$) bonding states, W_{pd}, and the number of valence electrons (VE's) to be accommodated in the bonding states, n_b, are also listed in Table III. It can clearly be seen that W_{occ} is systematically widened upon going from YAl_3 (9.34 eV) to $ZrAl_3$ (10.71 eV) to $NbAl_3$ (11.04 eV). With an increase in the number of VE's, on the other hand, $W_b(n_b)$ exhibits no systematic variation, but keeps nearly the same value of ~ 10 eV (12.3 electrons) [the maximum difference of $W_b(n_b) \leq 0.4$ eV (0.1 electrons) i.e., $\Delta W_b/W_b(\Delta n_b/n_b) \leq 4\%$ (1%)]. Considering the increasing number of VE's ongoing from YAl_3, $ZrAl_3$ to $NbAl_3$, the same size of $W_b(n_b)$ means that the bonding states have enough room to accommodate the VE's for YAl_3, but not for $NbAl_3$, with $ZrAl_3$ perhaps in between.

In fact, for YAl_3 all (12) VE's are being filled into the bonding states, and are nearly fully ($W_{occ}/W_b = 0.95$) occupying the bonding states; hence we expect that $L1_2$-YAl_3 is a strongly bonded structure as compared with $D0_{22}$. For $ZrAl_3$, W_{occ}/W_b ($=1.04$) is slightly larger

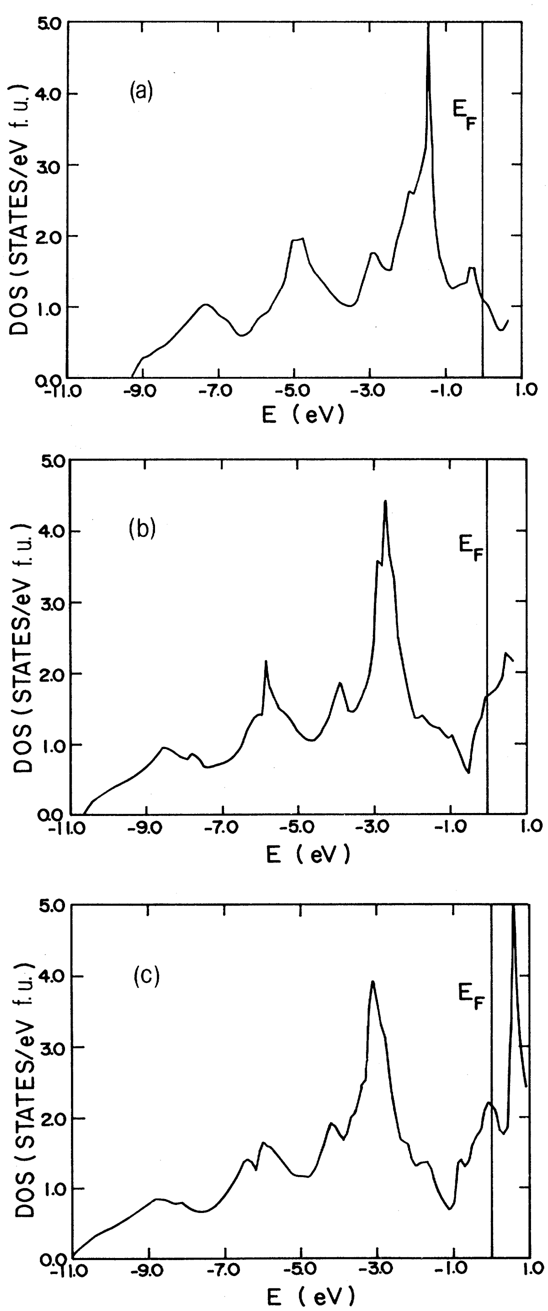

FIG. 2. The total density of states for (a) YAl_3, (b) $ZrAl_3$, and (c) $NbAl_3$.

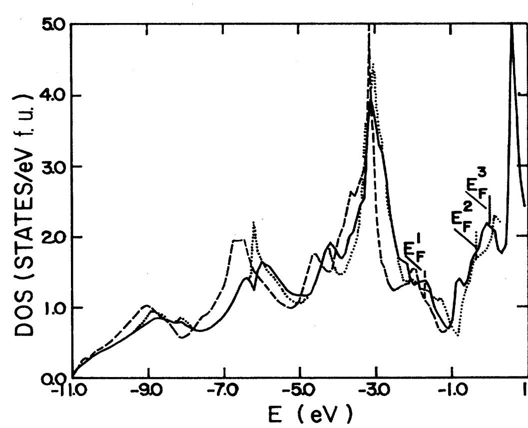

FIG. 3. Comparison of the total density of states for YAl_3, $ZrAl_3$, and $NbAl_3$; the bottom of the density of states of YAl_3 ($ZrAl_3$) has been shifted down 1.7 eV (0.3 eV) to coincide with that of $NbAl_3$; dashed line—YAl_3, dotted line—$ZrAl_3$, and solid line—$NbAl_3$. E_F^1, E_F^2, and E_F^3 denote the Fermi level of YAl_3, $ZrAl_3$, and $NbAl_3$, respectively.

than 1, which means that the bonding states of cubic $ZrAl_3$ already have no room for accommodating all its 13 VE's; $ZrAl_3$ can only accommodate the same number (12.36) as that of YAl_3, the extra 0.64 of a VE must occupy its nonbonding states. As a consequence, its E_F lies on the shoulder of nonbonding states, resulting in a metastable cubic phase of $ZrAl_3$. For cubic $NbAl_3$, the ratio of W_{occ}/W_b equaling 1.11 means that only 90% of the VE's can be accommodated into its bonding states; hence, the remaining 10% must go into the high-energy region of the nonbonding states. These results in the high instability of $L1_2$ with respect to[12] $D0_{22}$. Moreover, note that in Fig. 3 the overall features of the total DOS for these three cubic trialuminides resemble each other. Especially after we shift the bottom of the DOS of YAl_3 and $ZrAl_3$ to coincide with that of $NbAl_3$ the total DOS curves for these three systems fall onto the almost same curve (cf. Fig. 3); the distances W_{pd} from the bottom of the band to the peak of the *p*-*d* bonding states are nearly the same (=7.9 eV) for these three systems (cf. Table III).

The stability of the $L1_2$ phase decreases on going from YAl_3 and $ZrAl_3$ to $NbAl_3$, and eventually leads to a phase transformation to a $D0_{22}$ phase in $NbAl_3$. It thus appears that this can be understood in terms of band filling in the sense of a rigid-band model, because the valence electrons fill the bonding states up to E_F^1 in YAl_3, then begin to fill the nonbonding states up E_F^2 in $ZrAl_3$, and, finally, fill to a peak of the nonbonding states E_F^3 in $NbAl_3$. Therefore, the simple rigid-band concept appears to be adequate to explain the structural stability of these (*p*-*d* covalent) TM trialuminides.

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