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Aluminides of non-magnetic transition metals

The intermetallic compounds are of considerable interest from both the scientific and practical points of view [1, 2]. An important class of intermetallics is the aluminides of transition metals, and among them the simpler group of aluminides of non-magnetic transition metals. Interesting examples of the latter group represent, for instance, compounds VAl_{10} having anomalously large atomic volume [3] and heat capacity [4], Nb_3Al (having high superconductivity transition temperature) $NpAl_2$ and $NpAl_3$ (ferromagnetic compounds, although both components are non-magnetic [5]), Zr_3Al (a promising structural material for nuclear reactors), etc.

It was recently shown that a certain interrelation exists between the values of the deviations of atomic volume from additivity and the physical properties of the components [6–12]. The aim of the present note is to present the data of the deviations of atomic volumes from additivity (and in addition also the data of superconducting transition temperatures T_c [13]) for known aluminides of non-magnetic transition metals.

The percentage deviation (K) of atomic volume (V) from the sum of its components ($\Sigma\Omega$) was calculated by the formula [6–12]:

TABLE I Aluminides of transition metals with 3 and 4 outer electrons

Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)	Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)
YAl	CsCl	−2	—	HfAl	CrB	+3	—
$LaAl_3$	Ni_3Sn	−2	<1.3	ScAl	CsCl	+4	—
Zr_2Al	$CuAl_2$	−2	—	Sc_2Al	Ni_2In	+4	—
Hf_2Al	$CuAl_2$	−2	—	$LaAl_2$	Cu_2Mg	+4	3.2
$LaAl_4$	$BaAl_4$	−1	<1.1	Ti_3Al	Ni_3Sn	+4	—
LaAl	CeAl	0	<0.4	Zr_4Al_3	hexag.	+4	—
La_3Al_{11}	orthor.	0	<1.3	Hf_4Al_3	Zr_4Al_3	+4	—
YAl	CrB	+1	<1.1	Zr_2Al_3	orthor.	+4	—
Zr_5Al_3	W_5Si_3	+1	—	Hf_2Al_3	orthor.	+4	—
Zr_5Al_3	Mn_5Si_3	+1	—	$ZrAl_3$	tetrag.	+5	<1.0
Zr_3Al_2	tetrag.	+1	—	TiAl	AuCuI	+5	—
Hf_5Al_3	Mn_5Si_3	+1	—	$HfAl_3$	$ZrAl_3$	+5	—
Zr_5Al_4	Ti_5Ge_3	+2	—	$TiAl_3$	$TiAl_3$	+6	<1.0
La_3Al	Ni_3Sn	+2	6.2	$HfAl_3$	$TiAl_3$	+6	—
Hf_3Al_2	Zr_3Al_2	+2	—	$TiAl_2$	Ga_2Hf	+6	—
Y_3Al	Cu_3Au	+3	<1.1	YAl_3	Ni_3Sn	+6	—
Zr_3Al	Cu_3Au	+3	0.73	YAl_3	$BaPb_3$	+6	—
Y_2Al	$PbCl_2$	+3	<1.1	$ScAl_2$	Cu_2Mg	+7	<1.0
Y_3Al_2	Zr_3Al_2	+3	<1.1	$ZrAl_2$	$MgZn_2$	+7	<0.3
$LuAl_2$	Cu_2Mg	+3	<1.0	$ScAl_3$	Cu_3Au	+8	<4.2
Zr_2Al	Ni_2In	+3	—	$HfAl_2$	$MgZn_2$	+8	—
ZrAl	CrB	+3	—	YAl_2	Cu_2Mg	+9	<0.3

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TABLE II Aluminides of transition metals with 5, 6 and 7 outer electrons

Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)	Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)
VAl_{10}	cubic	−5	1.6	V_5Al_8	cubic	+3	—
$MoAl_{12}$	WAl_{12}	−1	<1.0	$MoAl_4$	WAl_4	+3	—
WAl_{12}	cubic	−1	—	Ta_3Al	σ-phase	+3	<1.0
$Re_{24}Al_5$	α-Mn	−1	3.3	Nb_2Al	σ-phase	+3	0.75
Ta_3Al	CsCl	0	1.6	Mo_3Al	β-W	+4	0.58
V_4Al_{23}	hexag.	0	<1.3	V_3Al	β-W	+5	11.1
V_7Al_{45}	monocl.	0	0.9	$Ta_{17}Al_{12}$	α-Mn	+5	—
$TcAl_{12}$	WAl_{12}	0	—	VAl_3	Al_3Ti	+7	<0.4
$ReAl_{12}$	WAl_{12}	0	<1.1	$TaAl_3$	Al_3Ti	+7	<1.2
Nb_3Al	CsCl	+1	3.1	$NbAl_3$	Al_3Ti	+7	0.64
Nb_3Al	β-W	+1	18.3	Tc_2Al	$MoSi_2$	+7	—
$TcAl_6$	$MnAl_6$	+1	—	Mo_3Al_8	monocl.	+8	—
$ReAl_6$	$MnAl_6$	+1	1.85	WAl_5	hexag.	+8	—
V_3Al	CsCl	+2	<2.5	$MoAl_5$	WAl_5	+8	<1.1
$ReAl_4$	Tricl.	+2	—	MoAl	CsCl	+9	—
Tc_2Al_3	trigon.	+2	—	$TcAl_4$	monocl.	+11	—
WAl_4	monocl.	+3	—				

$$K = \frac{\Sigma\Omega - V}{V} \times 100 = \frac{\Delta V}{V} \times 100 \qquad (1)$$

The crystallographic data were taken mainly from the same source as in previous notes [6–12].

Table I shows that in the aluminides of the transition metals with 3 and 4 electrons outside the inert gas shells, contraction is higher than that in transition metals compounds [6–12]. The contraction in general becomes larger in the aluminides of the transition metals of higher numbers of outer electrons (Tables II and III).

However, the compounds $MoAl_{12}$, WAl_{12}, $Re_{24}Al_5$, and Rh_2Al_9 do not show contraction and the compounds VAl_{10}, $PtAl_2$, Pu_3Al, PuAl, $PuAl_2$, etc. display relatively large expansion instead.

It seems reasonable to attribute the additional expansion in these compounds to the formation of closed electron subshells in the atomic cores outside the inert gas shells of the transition metals [6–12], so that the average number of bonding electrons per atom (n_k) is given by the formula:

$$n_k = n - n_0 - n_M \qquad (2)$$

where n is the average number of outer electrons, n_M that of electrons in the atomic core, responsible for the atomic magnetic moment and n_0 is the average number of electrons forming closed shells outside the inert gas shells of the transition metals [6–12]. According to the values of their atomic volumes pure Pd, Pt and Pu apparently display valency 6, i.e. $n_k = 6$ electrons provide the bonding and the rest, $n_0 = 4$ electrons in Pd, Pt and $n_0 = 2$ outer electrons in Pu, form closed

TABLE III Aluminides of transition metals with 8, 9 and 10 outer electrons

Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)
$PtAl_2$	CaF_2	−7	0.5
Rh_2Al_9	Co_2Al_9	0	—
Pd_2Al_3	Ni_2Al_3	0	—
Pt_2Al_3	Ni_2Al_3	+1	—
$RuAl_6$	orthor.	+3	—
$PtAl_4$	hexag.	+3	—
Os_4Al_{13}	monocl.	+4	5.5
Rh_2Al_5	Co_2Al_5	+4	—
Pt_8Al_{21}	tetrag.	+5	—
Pt_3Al	Cu_3Au	+6	—
Pt_2Al	Ni_2Si	+7	—
Ru_4Al_{13}	Fe_4Al_{13}	+8	<1.1
RuAl	CsCl	+8	—
Pt_3Al	Ti_3Cu	+8	—
Pd_2Al	$PbCl_2$	+8	—
PtAl	FeSi	+10	<0.3
Pt_5Al_3	Rh_5Ge_3	+10	—
Pd_5Al_3	Rh_5Ge_3	+10	—
Ru_2Al_3	Ni_2Al_3	+11	—
PdAl	CsCl	+12	—
$RuAl_2$	$TiSi_2$	+13	—
RhAl	CsCl	+13	—
OsAl	CsCl	+13	0.39
Os_2Al_3	tetrag.	+14	<1.1
$OsAl_2$	$MoSi_2$	+14	<1.1
IrAl	CsCl	+16	—

electron subshells with coupled spins [6–12]. However in compounds $PtAl_2$, Pu_3Al, PuAl and $PuAl_2$ the subshells of higher number of electrons ($n_0 = 6$ and $n_0 = 4$ in Pt and Pu respectively) are apparently formed with the corresponding reduction of the number of bonding electrons and an increase of atomic volume of the compounds. In compounds VAl_{10}, $MoAl_{12}$, WAl_{12}, $Re_{24}Al_5$, Rh_2Al_9 the subshells of $n_0 = 2$ electrons apparently are also formed in the atomic cores of transition metal atoms, i.e. for the atoms of V in this case $n_k = 3$, $n_0 = 2$; in Mo and W $n_k = 4$, $n_0 = 2$; in Rh $n_k = 7$, $n_0 = 2$, etc. In accomplishing interatomic bonding V in the compound VAl_{10} acts as Sc (the substitution for example of atomic volume of Sc in Formula 1 gives for the compound VAl_{10} the value $(\Delta V/V) \times 100 = 0$). It can be easily shown that such subshells are apparently formed in many compounds, for instance in $CoZr_2$, $CoTa_2$, CoU, $FeZr_2$, Ru_2Np, YCo_2, pure α-Mn, etc. [6–12].

It was shown that in YCo_2 [14] and in α-Mn [15] the magnetic susceptibility exhibits anomalous behaviour in strong magnetic fields. It is therefore desirable to extend these measurements to other compounds in which the formation of closed subshells is predicted. It should be noted that another possible explanation of the anomalies in YCo_2 has been proposed recently [16], but that this theory, based on the Fermi liquid model of magnetism, is unable to predict new compounds where the same effect may be observed.

The alternative method to reveal the existence of the closed subshell is the investigation of electron energy loss spectra, because a localized electron state (either with couple or magnetically ordered spins) gives rise to a dispersive line shape. For instance, Ni, which has both magnetic ($n_M = 0.6$) and closed ($n_0 = 2$) subshells [6–12] displays a larger percentage of localization than Mn, Fe and Co [17].

TABLE IV Aluminides of actinide metals

Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)
Pu_3Al	$CuTi_3$	−17	—
PuAl	cubic	−15	<1.5
$PuAl_2$	Cu_2Mg	−13	<1.2
$NpAl_2$	Cu_2Mg	−13	<1.5
$NpAl_3$	Cu_3Au	−11	<4.0
$NpAl_4$	UAl_4	−10	—
UAl_3	Cu_3Au	−10	<0.1
$PuAl_4$	UAl_4	−10	—
$PuAl_3$	Cu_3Al	−10	—
UAl_4	orthor.	−8	<2.0
UAl_2	Cu_2Mg	−8	<1.1
ThAl	CrB	−7	—
$ThAl_2$	AlB_2	−5	<0.4
Th_3Al_2	U_3Si_2	−5	2.6
Th_2Al	$CuAl_2$	−3	0.1
Th_2Al_7	orthor.	−2	—
$ThAl_3$	Ni_3Sn	−2	0.2

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