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Crystal Chemistry of AB_2 Structures.[1] I. Investigations on AB_2 Sections in the Ternary Systems Rare Earth–Aluminum–Silicon, –Germanium, and –Tin

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Seven ternary AlB_2-type phases were found in the systems La–Al–X, Ce–Al–X, and Nd–Al–X, where X stands for the elements Si, Ge, or Sn. The AlB_2-type structure is found to occur at valence electron concentrations between those required for the Laves phases and for the $ThSi_2$-type structure. The AB_2 structures investigated in the rare earth alloys form the following sequence with increasing valence electron concentrations: $MgCu_2 \rightarrow AlB_2 \rightarrow ThSi_2 \rightarrow GdSi_2$. The AlB_2-type phases are found to have anomalously higher volumes per atom than the $MgCu_2$- or $ThSi_2$-type phases.

Introduction

Numerous interesting crystal structures occur at the AB_2 stoichiometry in the binary systems of metallic elements. Among these the Laves phases form a major group in which 223 binary compounds crystallize.[3] The crystal chemistry and occurrence of structures with respect to valence electron concentration have been worked out thoroughly for the Laves phases[4,5] and for the disilicide structures,[6] $ZrSi_2$, $TiSi_2$, $CrSi_2$, and $MoSi_2$, etc. Nothing is known about the structures which occur between the Laves phases and the disilicide family of structures.

The binary rare earth dialuminides crystallize in the $MgCu_2$-type structure.[7] The lighter rare earth disilicides and digermanides have the $ThSi_2$- and $GdSi_2$-type structures. The AlB_2-type structure occurs only in the heavy rare earth disilicides and digermanides. In La–Si and Ce–Si as well as in all of the systems between La–Ge and Gd–Ge the AlB_2-type structure is not found. Vacancies at the atom sites of the nontransition element are present in the rare earth binary compounds with the AlB_2- and $GdSi_2$-type structures.[8] Some heavy rare earth distannides are found to possess the $ZrSi_2$-type structure.[9]

An investigation was initiated to study the crystal structures and phase equilibria in ternary alloys on the sections $(RE)Al_2$–$(RE)X_2$, where RE stands for the rare earths La, Ce, Nd, Gd, Y, and Er, and X is used for Si, Ge, or Sn. The Laves phase structures of the $(RE)Al_2$ compounds could be then linked to the $ThSi_2$- and $GdSi_2$-type disilicides through these series of compounds in which structural changes occur owing to variations in the valence electron concentrations (ratio of total valence electrons to number of atoms in the unit cell) and sizes of the atoms. It was of interest to develop a structural sequence connecting the Laves phase structures and the $ThSi_2$- and $GdSi_2$-type structures with respect to conventional valence electron concentration.[6] The results of this investigation are presented and discussed in this paper.

Experimental Section

The investigated alloys were arc melted under an argon atmosphere using elements of commercial purity (rare earth elements, 99.9+%; Al, 99.999+%; Si, Ge, and Sn, 99.99+%). After melting, the alloys were weighed. Those alloys containing Si and Ge could be obtained without any loss of material during melting. A small loss of Sn incurred in the alloys containing Sn was compensated for by weighing in a small excess of tin at the beginning. The alloys, wrapped in molybdenum foil, were annealed for 4 days at 1000° in evacuated quartz capsules and air cooled from that temperature. The crystal structures of the phases and the phase equilibria in the alloys were studied by powder X-ray diffraction techniques. The X-ray diffraction patterns of the alloy powders were prepared in a diffractometer or in a Guinier–de Wolff camera using Cu Kα (γ 1.5418 A) radiation. The lattice parameters of the different phases in Table I were obtained after minimizing the differences between the observed $\sin^2 \theta$ values, calculated from the diffraction angles θ, and the $\sin^2 \theta$ values, calculated using approximate lattice constants obtained from a few lines. These differences were minimized manually to less than 0.0005. The lattice constants are judged to be accurate to ± 0.005 A for values less than 10 A and to ± 0.01 A for values greater than 10 A.

Results

Substitution of Si, Ge, or Sn atoms for Al atoms in the $LaAl_2$, $CeAl_2$, and $NdAl_2$ phases led to compounds with the AlB_2-type structure. These compounds lie close to the $MgCu_2$-type dialuminides. No $MgZn_2$-type Laves phase was formed.

The lattice parameters, axial ratios, unit cell volumes, and mean atomic volumes of the newly discovered AlB_2-type phases are listed in Table I. The AlB_2-type ternary phases were found to possess the maximum mean atomic volumes.

Small homogeneous phase fields were found for all of the new AlB_2-type phases. Within the phase fields,

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Table I

Crystallographic Data for AB_2 Phases in the Investigated Ternary Sections

Alloy	Structure	a, A	c, A	c/a	Vol., A^3	A^3/atom
$LaSi_2$	$ThSi_2$	4.305	13.84	3.215	256.5	21.38
La_2AlSi_3	$ThSi_2$	4.303	14.21	3.302	263.1	21.93
LaAlSi	$ThSi_2$	4.284	14.56	3.400	267.2	22.27
$La_4Al_5Si_3$	$ThSi_2$	4.334	14.88	3.434	279.6	23.3
La_4Al_7Si	AlB_2	4.302	4.397	1.022	70.5	23.5
$La_{33.3}Al_{60}Si_{6.7}$	AlB_2	4.387	4.387	1.000	73.1	24.38
$La_{33.3}Al_{64.7}Si_2$	$MgCu_2$	8.130			537.4	22.40
$LaAl_2$[a]	$MgCu_2$	8.145			540.4	22.52
$LaGe_2$[b]	$ThSi_2$	4.330	14.23	3.286	266.8	22.23
LaAlGe	$ThSi_2$	4.307	14.72	3.417	273.0	22.75
La_2Al_3Ge	AlB_2	4.338	4.390	1.012	71.5	23.84
La_4Al_7Ge	AlB_2	4.397	4.397	1.000	73.6	24.55
La_4Al_7Sn	AlB_2	4.474	4.397	0.983	76.2	25.40
$CeSi_2$[c]	$ThSi_2$	4.150	13.87	3.344	239.0	19.90
Ce_2Al_3Si	$ThSi_2$	4.280	14.90	3.480	272.8	22.73
$Ce_8Al_{13}Si_3$	AlB_2	4.315	4.298	0.996	69.3	23.10
$Ce_{33.3}Al_{64.7}Si_2$	$MgCu_2$	8.040			520.0	21.66
$CeAl_2$[a]	$MgCu_2$	8.057			523.0	21.80
$Ce_8Al_{13}Ge_3$	AlB_2	4.350	4.290	0.986	70.3	23.43
$Ce_{33.3}Al_{64.7}Ge_2$	$MgCu_2$	8.034			518.5	21.60
$Ce_8Al_{13}Sn_3$	AlB_2	4.454	4.284	0.962	73.6	24.53
$Ce_{33.3}Al_{65.7}Sn$	$MgCu_2$	8.050			521.7	21.74
$NdSi_2$	$ThSi_2$	4.162	13.58	3.260	235.2	19.60
Nd_2Si_3[8]	AlB_2	3.940	4.258	1.080	57.2	21.45
$Nd_4Al_5Si_3$	AlB_2	4.276	4.204	0.983	66.5	22.18
Nd_4Al_7Si	$MgCu_2$	7.986			509.2	21.22
$NdAl_2$[a]	$MgCu_2$	8.000			512.0	21.33
Nd_2Ge_3	$ThSi_2$	4.164	14.09	3.384	244.3	20.36
$NdGe_2$[b]	$ThSi_2$	4.240	13.90	3.278	250.0	20.83
Nd_2Al_3Ge	AlB_2	4.298	4.210	0.980	67.4	22.45
$Nd_8Al_{13}Ge_3$	AlB_2	4.308	4.204	0.976	67.6	22.52
$Nd_4Al_5Sn_3$	AlB_2	4.450	4.179	0.939	71.6	23.88
$GdSi_2$[d]	$GdSi_2$	a = 4.080, b = 3.996	13.41		218.8	18.23
	$ThSi_2$[d]	4.100	13.61	3.320	228.8	19.07
GdAlSi	$ThSi_2$	4.131	14.44	3.496	246.6	20.55
$Gd_{33.3}Al_{58.3}Si_{8.4}$	$MgCu_2$	7.860			485.5	20.23
$GdAl_2$[a]	$MgCu_2$	7.901			493.0	20.54
Gd_2Ge_3	$ThSi_2$	4.077	13.73	3.367	228.2	19.02
$GdGe_2$[b]	$ThSi_2$	4.120	13.72	3.330	232.9	19.41
GdAlGe	$ThSi_2$	4.148	14.46	3.486	248.7	20.73
$Gd_{33.3}Al_{58.3}Ge_{8.4}$	$MgCu_2$	7.860			485.5	20.23

[a] See ref 7. [b] E. I. Gladyshevskii, *Zh. Strukt. Khim.*, **5**, 568 (1964). [c] W. H. Zachariasen, *Acta Cryst.*, **2**, 94 (1949). [d] J. A. Perri, E. Banks, and B. Post, *J. Phys. Chem.*, **63**, 2073 (1959).

both the mean atomic volumes and the axial ratios changed appreciably with variations in composition. With decreasing Al content, the *a* parameter of the AlB_2-type phases decreases rapidly and the *c* parameter changes by a very small amount so that the axial ratio increases. For example, the axial ratio changed from 1.00 in Al-rich compounds to 1.022 in Si-rich compounds in the AlB_2-type alloys of the $LaAl_2$–$LaSi_2$ section (Figure 1). The mean atomic volume decreases with decreasing Al content within the phase field. Similar variations in the other alloys can be studied in Table I.

The disilicides and digermanides of La, Ce, and Nd possess both $ThSi_2$- and $GdSi_2$-type structures. Substitution of Al for Si or Ge in these compounds leads to the extensions of the $ThSi_2$-type phases into the ternary systems. The $ThSi_2$-type phases were found to dissolve as much as 60 atomic % Al in the structure. The lattice parameters, axial ratios, and cell volumes changed considerably.

The variations in the unit cell characteristics of $LaSi_2$ ($ThSi_2$-type) are shown in Figure 1. The *a* parameter remains constant initially, then drops with increasing Al content, and at Al-rich concentrations increases

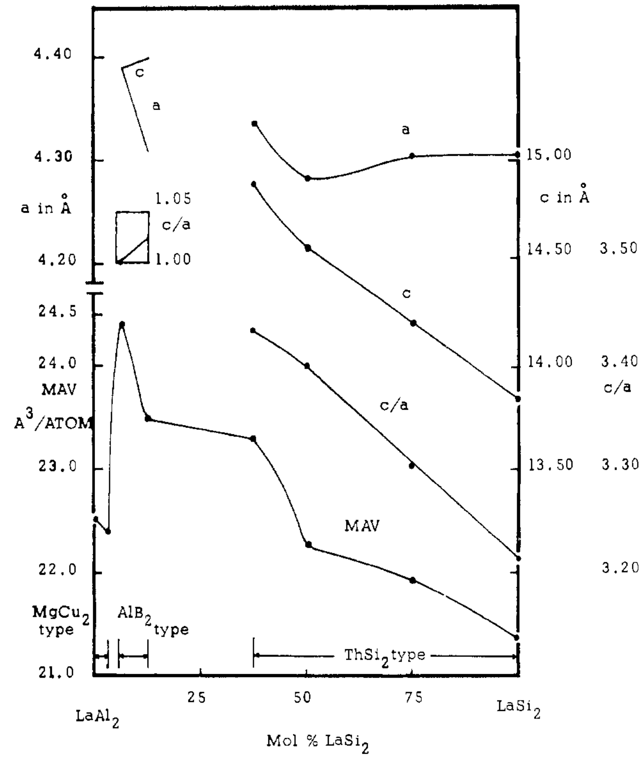

Figure 1.—Variations in the lattice parameters, axial ratios, and the mean atomic volumes of the phases on the $LaAl_2$–$LaSi_2$ quasibinary section.

enormously. The *c* parameter increases, on the contrary, almost linearly. The axial ratio increases with increasing Al content. The mean atomic volume increases slowly at the beginning and then very rapidly to the value of the Si-rich AlB_2-type ternary phase as higher Al concentrations are reached. Similar results, obtained for other $ThSi_2$-type phases, can be found in Table I.

Alloys lying on the $GdAl_2$–$GdSi_2$ section showed that the $GdAl_2$ ($MgCu_2$-type) phase is in equilibrium with a $ThSi_2$-type phase rather than with the AlB_2-type phase on this section. The defective AlB_2-type phase of the Gd–Si system was not found to extend to the true AB_2 stoichiometry. Similarly, the $MgCu_2$-type phase, $GdAl_2$, was in equilibrium with the $ThSi_2$-type phase, $GdGe_2$, in the $GdAl_2$–$GdGe_2$ alloys.

Sn-rich alloys were found to oxidize quickly in air and were not studied owing to the lack of facilities for preparation and examination under vacuum. Our investigation showed that no AlB_2-type phase was formed on the $GdAl_2$–$GdSn_2$ section. The alloys with more than 10 atomic % Sn were found to oxidize quickly in air. A ternary phase was detected on the $ErAl_2$–$ErSn_2$ section. Two ternary phases were obtained on the YAl_2–YSn_2 section. Their structures could not be identified. The Er compounds were stable in air, while the Y compounds oxidized slowly.

Alloys on the $ErAl_2$–$ErSi_2$, $ErAl_2$–$ErGe_2$, YAl_2–YSi_2, and YAl_2–YGe_2 sections gave rise to complicated powder patterns, which showed the occurrence of new ternary phases.

Discussion

The rare earth disilicides crystallize in the $ThSi_2$-, $GdSi_2$-, and AlB_2-type structures at the ideal AB_2 stoichiometry or close to it. Compounds crystallizing in these structures at nonstoichiometric compositions are found to contain vacancies in the B atom positions.

Substitution of Al for Si extends the AlB_2- and the $ThSi_2$-type disilicides into the ternary system. The $GdSi_2$-type structure is stable only in the binary alloys. It is known that the $GdSi_2$-type structure is derived from the $ThSi_2$-type structure by slight structural distortions. Also continuous transformation from the $ThSi_2$-type to the $GdSi_2$-type has been found in the La–Si system.[10] Our results indicate that the orthorhombic distortion is not retained in ternary alloys and the $ThSi_2$-type structure extends deep into the ternary systems. A similar result has been obtained in the Ti–Al–Si system for the $ZrSi_2$-type ternary phase.[11]

The AlB_2-type structure does not occur in the lanthanum and cerium disilicides. It is not found in the digermanides of the light rare earths starting from La to Gd. No rare earth distannide is known to possess the AlB_2-type structure. Our results show that the AlB_2-type structure is stabilized in several ternary compounds of the rare earths on the (RE)Al_2–(RE)Si_2, –(RE)Ge_2, and –(RE)Sn_2 sections. Substitutions of large amounts of Al for Si or Ge in the $ThSi_2$-type phases leads to a change in the structure to the AlB_2-type.

It is generally believed that Al, since it has only three valence electrons, reduces the over-all valence electron concentration when it is added to the rare earth disilicides or digermanides. This assumption can be valid and applicable especially for those alloys which are rich in nontransition metal atoms. On this basis we hypothesize that a reduction in the valence electron concentration of the $ThSi_2$-type compounds leads to the stabilization of the AlB_2-type structure.

Substitution of Si, Ge, or Sn for Al atoms in the (RE)-Al_2 compounds stabilizes the AlB_2-type structure. In the binary and ternary alloys of group IV and V transition elements with similar nontransition elements the $MgZn_2$-type occurs. Hence, it can be concluded that the $MgZn_2$-type occurs at higher valence electron concentrations than those for the $MgCu_2$-type. However, an increase in the valence electron concentration through substitution of Si, Ge, or Sn for Al in the (RE)-Al_2 compounds does not stabilize the $MgZn_2$-type structure.

Alloys on the $GdAl_2$–$GdSi_2$ section indicate that the defects in the AlB_2-type binary silicide Gd_3Si_5 are not removed on alloying with Al. No AlB_2-type phase is found on the $GdAl_2$–$GdGe_2$ and $GdAl_2$–$GdSn_2$ sections. In the former section the $MgCu_2$-type phase, $GdAl_2$, is found to be in equilibrium with the $ThSi_2$-type phase, $GdGe_2$.

The occurrence of the Laves phases in transition metal alloys that have valence electron concentrations close to those of the transition metal disilicides is now better understood.[12] The partial structural sequence with respect to increasing valence electron concentration is obtained

$$MgCu_2 \longrightarrow (MgZn_2) \longrightarrow AlB_2 \longrightarrow ThSi_2 \longrightarrow GdSi_2$$

The AlB_2-type ternary phases possess maximum volumes per atom; this quantity decreases as the structure changes from the AlB_2 type on either side of the structural sequence. This anomaly cannot be explained on the basis of normal atomic volumes of Al or Si atoms, deduced from the pure elemental structures. More work needs to be done in order to account for this anomalous increase in volume in the AlB_2-type ternary phases.

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Coordination Chemistry of Tungsten Dioxodichloride

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A series of complex compounds of tungsten(VI) dioxodichloride of the types $WO_2Cl_2 \cdot 2L$ and $WO_2Cl_2 \cdot B$, where L = dimethylformamide, triphenylphosphine oxide, hexamethylphosphoramide, dimethyl sulfoxide, tetramethylene sulfoxide, or methyl cyanide and B = bipyridyl or phenanthroline, have been prepared by one or more of three preparative methods. The infrared and ultraviolet spectra of these compounds have been recorded and the results are discussed. The properties of two tungsten(V) oxotrichloride complexes formed under slightly different reaction conditions have also been examined.

Introduction

The coordination chemistry of molybdenum dioxodihalides has been examined extensively. Thus neutral complexes of the general formulas $MoO_2X_2 \cdot 2L$ (L = monodentate) and $MoO_2X_2 \cdot B$ (B = bidentate, X = Cl or Br) have been prepared by the reaction of MoO_2X_2 with ligands, with or without a solvent,[1-4] by halogen

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