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Ternary FeB- and CrB-Type Phases with Yttrium, Lanthanum, and Some Rare Earths¹

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Rare earth equiatomic phases with similar CrB- or FeB-type structures form complete solid solutions with each other if the non rare earth component is the same. GdNi and ErSi do not form continuous series of solid solutions, although their structures are similar. The structures of six new ternary phases were determined. The variations in the characteristics of the trigonal prisms in the CrB-type phases are analyzed.

Introduction

The majority of the rare earth binary equiatomic alloys crystallize in the CsCl, CrB, FeB, or NaCl types of crystal structures. Of these, the CrB and FeB structures are known to occur in two different branches:² branch I: the rare earth alloys with non-transition elements of the third and fourth groups (Al, Ga, Si, Ge, etc.); branch II: The rare earth equiatomic compounds with transition elements of the ninth and tenth groups (Co, Rh, Ni, Pd, Pt, etc.). These two branches are separated by the CsCl-type structure, which occurs in equiatomic alloys of the rare earths with the nontransition elements of the first and second groups (Cu, Ag, Zn, Cd, etc.).³

The structural characteristics of the rare earth alloys which have FeB and CrB structures in both branches have been discussed by Hohnke and Parthé.² Excellent figures to illustrate the crystal structures of the CrB, FeB, and MoB structure types and the interrelationships between these crystal structures are found in the paper by Hohnke and Parthé.² The trigonal prisms—the building blocks in these structures—have different prism ratios (ratio of height to edge of base) in the two branches. This ratio, determined from the lattice constants of the compounds, is equal to a/c for CrB-type compounds (space group Cmc₂m) and $(1/2b)[a^2 + (1 - 4Z_{Fe})^2C^2]^{1/2}$ for FeB-type compounds² (space group Pnma). The prism ratio is greater than 1 for branch I compounds and less than 1 for branch II compounds. No binary rare earth equiatomic compound with either an FeB or a CrB structure is known in which the prism ratio is unity as it is in ZrSi(CrB) and ZrAlSi(CrB).^{4,5}

This paper reports on the structural characteristics of some selected ternary alloys of group III transition elements. A research project was initiated to investigate mainly the occurrence of the FeB- and CrB-type structures in these alloys. The isostructural compounds of both branches were alloyed together in vary-

ing proportions to study solid solubility of alloys with similar structures. For one element of each compound an element of slightly different valence was substituted and an analysis of the resultant crystal structures was made. The effects of ternary additions on the trigonal-prism ratios in the binary phases were also investigated.

A further question was whether the pseudo-tetragonal CrB-type^{4,5} or the MoB-type⁶ structures could be stabilized in the rare earth ternary alloys.

Experimental Method

La, Y, and the rare earths Ce, Nd, Gd, Ho, Er (of commercial purity 99.9+%) and Zr (reactor grade 99.99+%) were alloyed with Fe, Ni, Al, Si (99.99+%), and Cu (99.92+%) by melting in an arc furnace under argon atmosphere. Negligible loss of material was encountered during melting, and hence the chosen compositions were assumed to be present in the alloys. No chemical analysis of the alloys was carried out. The alloys could be broken easily by hammering. Pieces of each alloy were wrapped in molybdenum foil, sealed in evacuated quartz tubes, and annealed for 3 days at 1000°. After annealing, the specimens were air cooled.

The crystal structures and phase relationships in the alloys (in both the as-cast and the annealed state) were studied by analysis of powder X-ray diffraction photographs taken with a diffractometer or with a Guinier-de Wolff camera. Only for a few alloys was a metallographic examination undertaken. The lattice parameters of the phases, listed in Table I, were calculated after minimizing manually for all the lines the differences between the $\sin^2 \theta$ values from observed θ and the $\sin^2 \theta$ values that were calculated from approximate lattice constants. The differences were reduced to less than 0.0005. The reported values are accurate to $\pm 0.005 \text{ \AA}$, for lattice constants less than 10 \AA , and to $\pm 0.01 \text{ \AA}$ for those greater than 10 \AA . Further precision was not attempted.

Results

The phase equilibria in some of the investigated alloys are represented in Figure 1. The possible homogeneity ranges for the ternary phases, which were found to occur in some of these sections, can be inferred from this figure. The exact limits of the phase boundaries were not determined. The crystal structures of the binary phases are given after each phase in brackets. For ErSi both the CrB I and FeB I structures are reported.² However, only the CrB I modification was obtained in this investigation. Similarly only the CrB II modification was obtained repeatedly in the

(1) Research supported by the sustaining research grant of the National Aeronautics and Space Administration (NASA) to the Louisiana State University, under Grant 19-001-024.

(2) D. Hohnke and E. Parthé, *Acta Cryst.*, **20**, 572 (1966).

(3) O. D. McMasters and K. A. Gschneidner, Jr., *Nucl. Met. Ser.*, **10**, 92 (1964).

(4) O. Schob, H. Nowotny, and F. Benesovsky, *Planseeber. Pulvermet.*, **10**, 65 (1962).

(5) A. Raman and K. Schubert, *Z. Metallk.*, **56**, 45 (1965).

(6) R. Kiessling, *Acta Chem. Scand.*, **1**, 893 (1946); *Struct. Rept.*, **11**, 51.

TABLE I
 STRUCTURAL CHARACTERISTICS OF THE RARE EARTH TERNARY EQUIATOMIC COMPOUNDS

Compound	Structure type	Lattice constants, Å			Prism ratio (height/base) (a/c) _{CrB}	Cell vol, Å ³	MAV, Å ³ /atom
		a	b	c			
(a) LaNi	CrB II	3.906	10.77	4.372	0.893	184.0	23.00
La ₃₇ Gd ₁₃ Ni ₅₀	CrB II	3.852	10.60	4.350	0.886	177.7	22.21
La ₂₅ Gd ₂₅ Ni ₅₀	CrB II	3.825	10.45	4.352	0.879	174.0	21.75
La ₁₃ Gd ₃₇ Ni ₅₀	CrB II	3.767	10.43	4.280	0.880	168.1	21.01
GdNi	CrB II	3.764	10.31	4.210	0.894	163.3	20.40
(b) YNi ^a	FeB II	7.151	4.124	5.513		162.6	20.33
Y ₃₇ Er ₁₃ Ni ₅₀	FeB II	7.107	4.130	5.483		161.0	20.13
Y ₂₅ Er ₂₅ Ni ₅₀	FeB II	7.075	4.118	5.450		158.7	19.84
Y ₁₃ Er ₃₇ Ni ₅₀	FeB II	7.000	4.114	5.433		156.4	19.55
ErNi	FeB II	6.946	4.100	5.368		153.0	19.12
(c) LaSi	FeB I	8.380	3.990	6.024		201.4	25.18
La ₃₇ Gd ₁₃ Si ₅₀	FeB I	8.308	3.960	5.972		196.4	24.55
La ₂₅ Gd ₂₅ Si ₅₀	FeB I	8.178	3.946	5.880		189.7	23.71
La ₁₃ Gd ₃₇ Si ₅₀	FeB I	8.015	3.910	5.813		182.1	22.76
GdSi	FeB I	7.935	3.856	5.730		175.4	21.93
(d) YSi	CrB I	4.251	10.53	3.826	1.11	171.2	21.40
Y ₂₅ Er ₂₅ Si ₅₀	CrB I	4.233	10.44	3.804	1.11	168.0	21.00
ErSi	CrB I	4.190	10.35	3.778	1.11	163.8	20.48
(e) NdNi	CrB II	3.802	10.47	4.335	0.877	172.5	21.56
Nd ₃₇ Zr ₁₃ Ni ₅₀	CrB II	3.773	10.39	4.341	0.869	170.2	21.28
Nd ₅ Zr ₄₅ Ni ₅₀	CrB II	3.260	9.833	4.100	0.795	131.4	16.43
ZrNi ^b	CrB II	3.268	9.937	4.101	0.797	133.2	16.65
(f) La(Zr)Si	FeB I	8.380	3.99	6.024		201.4	25.18
Zr(La)Si	CrB I	3.738	9.875	3.738	1.00	138.0	17.25
ZrSi ^c	CrB I	3.780	10.05	3.780	1.00	143.6	17.95
Zr ₃₃ Al ₂₃ Si ₄₄ ^c	CrB I	3.745	9.863	3.745	1.00	138.3	17.29
(g) GdNi	CrB II	3.764	10.31	4.210	0.894	163.3	20.40
GdNi ^d	FeB II	6.931	4.353	5.248		171.6	21.45
Gd ₂ Ni ₃ Cu ^e	FeB II	7.033	4.230	5.410		160.9	20.11
Gd ₂ NiCu ^e	FeB II	7.033	4.412	5.490		170.4	21.30
GdCu	CsCl	3.503		43.0	21.50
(h) ErNi	FeB II	6.946	4.100	5.368		153.0	19.30
Er ₂ NiCu ^e	CrB I	4.225	10.47	3.851	1.10	170.3	21.30
Er ₄ NiCu ₃ ^e	CrB I	4.193	10.35	3.787	1.11	164.4	20.55
ErCu	CsCl	3.432		40.4	20.20
(i) GdSi	FeB I	7.935	3.856	5.730		175.4	21.93
Gd ₄ AlSi ₃ ^e	CrB I	4.322	10.66	3.866	1.12	178.2	22.28
GdAl ^f	ErAl	5.656	5.888	11.527		384.0	24.00
(j) ErSi ^g	FeB I	7.772	3.785	5.599		164.7	20.59
ErSi	CrB I	4.190	10.35	3.778	1.11	163.8	20.48
Er ₄ AlSi ₃ ^e	CsCl	3.388		38.9	19.45
Er ₂ AlSi ^e	FeB II	6.865	4.307	5.350		158.2	19.78
Er ₄ Al ₃ Si ^e	FeB II	6.910	4.223	5.395		157.4	19.68
ErAl ^f	ErAl	5.570	5.801	11.272		364.2	22.76
(k) ErNi	FeB II	6.946	4.100	5.368		153.0	19.12
Er ₄ Ni ₃ Si ^g	CrB II	3.735	10.20	4.082	0.915	155.5	19.44
ErSi	CrB I	4.190	10.35	3.778	1.11	163.8	20.48

^a A. E. Dwight, Report ANL-6099, Argonne National Laboratory, Argonne, Ill., 1959. ^b M. E. Kirkpatrick, D. M. Bailey, and J. F. Smith, *Acta Cryst.*, **15**, 252 (1962). ^c See ref 5. ^d N. C. Baenziger and J. L. Moriarty, Jr., *Acta Cryst.*, **14**, 946 (1961). ^e Phases discovered in this investigation. The lattice parameters for the binary phases for which no reference is given have been obtained in the present investigation. ^f K. H. J. Buschow, *J. Less-Common Metals*, **8**, 209 (1965). ^g See ref 2.

alloy Gd₅₀Ni₅₀. The other binary phases pertinent to this paper, excepting ZrSi, are known to possess only one form and are represented accordingly. The tentative extensions of the binary phases into the respective sections were judged from the relative intensities of the X-ray diffraction patterns of the phases in one or more two-phase alloys and are given in the figure.

Table I contains the structural data of several alloy phases. The lattice constants of the binary phases are also included. The measured and calculated X-ray

densities of some of the newly discovered phases are given in Table II.

The rare earth alloys with similar structures (either CrB or FeB) dissolve freely in each other, if they belong to the same branch. Thus complete mutual solid solubility was established in the following sections: LaNi(CrB)-GdNi(CrB), ErNi(FeB)-YNi(FeB), LaSi(FeB)-GdSi(FeB), and ErSi(CrB)-YSi(CrB).

GdNi and ErSi, two selected representatives from the two branches, did not form continuous solid solutions with each other, although their structures are

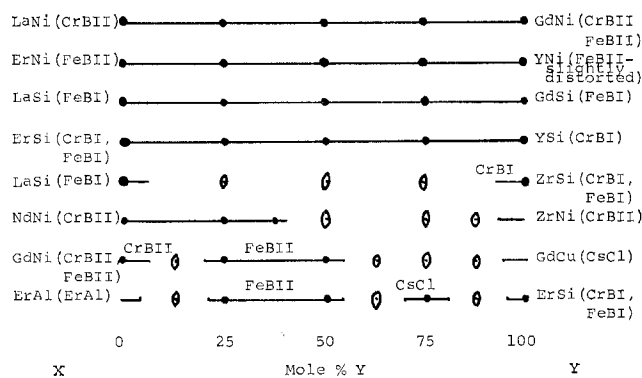


Figure 1.—Pictorial representation of the phase equilibria in the investigated alloys. The limits of extensions of the phases are tentative: ●, single phase; ○, two phases.

TABLE II
MEASURED AND CALCULATED X-RAY DENSITIES
OF THE NEW TERNARY PHASES

Phase	Density, g/cm ³	
	Calcd from X-ray data	Measd (±0.1 g/cm ³)
Er ₂ AlSi	8.179	7.98
Er ₄ Ni ₃ Si	9.325	9.15
Er ₄ NiCu ₃	9.277	9.10
Er ₂ NiCu	8.908	8.90
Er ₄ Ni ₃ Cu	...	9.44
Gd ₂ NiCu	8.501	8.47
Gd ₄ Ni ₃ Cu	8.953	8.92
Gd ₄ AlSi ₃	6.887	6.70

similar. No appreciable solid solubility of one in the other was found. The powder diffraction patterns of the alloys in this section were complex.

Similarly structured equiatomic alloys of zirconium did not form continuous series of solid solutions with the rare earth alloys. Two-phase equilibria were found in the alloys of the LaSi(FeB)–ZrSi(FeB,⁷ CrB^{4,5}) and NdNi(CrB)–ZrNi(CrB)⁸ sections. In the first section, the ZrSi(CrB) phase was found to be in equilibrium with LaSi(FeB) and no appreciable solid solubility of Zr in LaSi was observed. However, Zr substitutes for about 20% of the atoms at the Nd sites in NdNi, with the unit cell thereby contracting. Nd and La dissolve by less than 5 atom % at the Zr sites in ZrNi and ZrSi, respectively.

Variations in Valence Electron Concentrations (VEC).

—The VEC of the rare earth alloys was varied in the low regions by the addition of RE–Cu to the RE–Ni compounds and of RE–Al to the RE–Si compounds (RE = a rare earth element). Cu and Al were assumed to reduce the over-all VEC when substituted for Ni and Si, respectively, in the rare earth alloys. The arguments in favor of this assumption are brought forth in another paper by the author.⁹

GdNi(CrB)–GdCu(CsCl)¹⁰ Section.—

(7) H. Schachner, H. Nowotny, and H. Kudielka, *Monatsh. Chem.*, **85**, 1142 (1954).

(8) M. E. Kirkpatrick, D. M. Bailey, and J. F. Smith, *Acta Cryst.*, **18**, 252 (1962).

(9) A. Raman and H. Steinink, *ibid.*, **22**, 688 (1967).

(10) A. E. Dwight and M. V. Nevitt, Report ANL-6099, Argonne National Laboratory, Argonne, Ill., 1959.

GdNi was found to possess only the CrB-type structure.¹¹ However, a ternary phase with an FeB-type structure and lattice characteristics resembling those of ErNi(FeB) was found in this section. The ternary phase was found in a wide, homogeneous phase field between the two stoichiometries Gd₄Ni₃Cu and Gd₂NiCu and was found to be in equilibrium with the CsCl- and CrB-type binary phases. The unit cell volume first decreases as the structure changes to the FeB type: it then increases as more and more Cu atoms replace Ni atoms (see Table I).

ErNi(FeB)–ErCu(CsCl)¹⁰ Section.—A ternary phase with the CrB I-type structure (as in ErSi) was observed in the alloys of this section. The alloy Er₅₀Ni₂₅Cu₂₅ was single phased and contained the CrB-type ternary phase. The ternary phase was found to occur between the stoichiometries Er₂NiCu and Er₈Ni₃Cu₅ and was in equilibrium with the CsCl-type phase in the Cu-rich alloys. The lattice parameters of the ternary phase changed considerably with the composition (see Table I).

In ternary alloys, the unit cell volume of ErNi increases until the Ni-rich CrB-type ternary phase is reached. Within the CrB-type phase field, a further increase in the Cu content reduces the cell volume, which ultimately drops to the value of ErCu. Thus the characteristics are different from those of Gd–Ni–Cu alloys.

GdSi(FeB)–GdAl(ErAl)¹² Section.—In this section, a ternary phase of composition Gd₅₀Al₁₃Si₃₇, with the CrB I-type structure (as in ErSi), was found. The unit cell volume of the CrB-type phase was larger than that of the FeB-type binary phase. Another unidentified phase was present in Al-rich alloys.

ErSi(CrB)–ErAl(ErAl)¹² Section.—Two ternary phases were found in this section. One of them, designated as Er₄AlSi₃, had the CsCl-type structure, while the Al-rich alloys Er₅₀Al₂₅Si₂₅ and Er₅₀Al₃₇Si₁₃ had an FeB-type ternary phase (as in ErNi). Considerable lattice parameter changes indicated that this ternary phase occurred in a wide homogeneous phase field. In addition, the lines of an unidentified phase (probably due to impurities) were present in all the diffraction patterns.

The mean atomic volume, MAV (average volume in the unit cell per atom), decreases as the structure changes from the CrB to the CsCl type but further increases as the structure changes to the FeB type. Within the FeB-type phase field the MAV decreases with increasing Al content. The MAV, as calculated from the literature data,¹² attains the maximum value in ErAl (see Table I).

ErNi(FeB)–ErSi(CrB) Section.—A CrB-type ternary phase (similar to GdNi) was found in the alloy Er₅₀Ni₃₇Si₁₃. The patterns of the Si-rich alloys were complex.

(11) A. E. Dwight, R. A. Conner, Jr., and J. W. Downey, *Acta Cryst.*, **18**, 835 (1965).

(12) K. H. J. Buschow, *J. Less-Common Metals*, **8**, 209 (1965).

Discussion

An FeB II-type phase has been found to occur in the GdNi–GdCu section. This phase possesses similar lattice parameters as reported by Baenziger and Moriarty¹³ for the GdNi(FeB II) phase. In the present investigation alloys of nominal composition $Gd_{50}Ni_{50}$ have shown only the CrB-type structure.¹¹ Also, the FeB II-type phase obtained in the ternary alloys was found to be in equilibrium with the CrB II-type phase. Since no trace of the FeB II-type phase was detectable in the binary alloy, the author believes that it is a true ternary phase. ErNi possesses only the FeB II-type structure. Hence the CrB II-type phase obtained in the ErNi–ErSi section is a ternary one. Likewise the CrB I-type phase found in the GdAl–GdSi section is also a true ternary one, since the CrB I-type structure does not occur in GdSi. The other newly found phases are inferred to be ternary ones since their structural characteristics are different from those of the binary phases of the respective sections.

Er and Si (in ErSi) do not substitute for Gd and Ni, respectively in GdNi, even though the structures of GdNi and ErSi are similar. In either GdNi or ErSi, the prism characteristics of one are not influenced on alloying with the other. It is highly probable that the other phases with particular prism characteristics from one branch do not modify the prism characteristics of phases from the other branch when they are alloyed.

In the ternary alloys of the LaNi–GdNi section, the prism ratio reduces to minimum values at about the

middle of the section, although both LaNi and GdNi have nearly the same prism ratios. However, in the YSi–ErSi section the prism ratio remains fairly constant.

The phases of the group IV transition elements with similar structures generally have smaller prism ratios than the rare earth phases. When Zr substitutes for Nd in NdNi, the prism ratio decreases further, but not continuously, to the value of ZrNi.

The maximum prism ratio (0.915) for a phase in branch II is obtained, for the CrB-type ternary phase, in the ErNi–ErSi section. The Er_2NiCu (CrB I) phase has the minimum prism ratio (1.10) among phases with the CrB-type structure in branch I. In general, the ternary phases with the CrB-type structure have prism ratios that do not differ widely from those of the binary phases within the same branch.

In the present investigation, the prism ratio in the CrB-type phases is not found to be affected appreciably by alloying with elements which reduce the valence electron concentrations. Several other sections (not reported here) indicate that phases with possible new structures are stabilized before the prism ratio is brought to unity. In this respect, $ZrSi(CrB I)^{4,5}$ and $ZrAlSi(CrB)^{4,5}$ with square prism sides (prism ratio = 1), are apparently unique in branch I. No MoB-type phase has yet been detected in ternary alloys.

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(13) N. C. Baenziger and J. L. Moriarty, Jr., *Acta Cryst.*, **14**, 946 (1961).

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Electronic Spectral Studies of Some Uranium(V) Compounds¹

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The following solid compounds were prepared and characterized in inert atmospheres: $MUCl_6$ ($M = Rb$ and $(n-C_8H_7)_4N$), both new compounds in regard to the cation present; $UCl_5 \cdot SOCl_2$; $UCl_5 \cdot PCl_5$; and $UCl_5 \cdot TCAC$ (TCAC = trichloroacrylyl chloride, $Cl_2C=CClCOC(=O)Cl$), a new compound. In addition, solutions of UCl_5 in CCl_4 and $SiCl_4$ were prepared. Infrared spectra were obtained. Electronic spectra in the near-ir and visible region were obtained for the $MUCl_6$ compounds dissolved in $SOCl_2$; for $UCl_5 \cdot TCAC$ dissolved in $SOCl_2$, C_6H_6 , CS_2 , and CCl_4 ; for $UCl_5 \cdot SOCl_2$ dissolved in $SOCl_2$ and CCl_4 ; and for UCl_5 in CCl_4 and $SiCl_4$. Electronic as well as vibronic band assignments have been made for these $5f^1$ electronic systems and several of the vibrational frequencies of the UCl_6^- species have been deduced from the electronic spectra. The first esr spectra for pure U(V) compounds, obtained with powdered samples, are reported, and the average g values are all 1.1.

Introduction

The literature available on the chemistry of uranium(V) is meager when compared to the voluminous data collected for the other three oxidation states (III, IV,

and VI) of the element. The lack of information about the quinquevalent state is not surprising in light of the large inherent thermodynamic instability of this oxidation state relative to the quadri- and hexivalent states, leading to rapid and easy disproportionation and the ready oxidation to the latter state. In spite of its instability however, the U(V) entity is chemically and

(1) Abstracted in part from the Ph.D. thesis of J. D. Ortego, Louisiana State University, 1968.