

The Crystal Structures of Rare-Earth Monosilicides*

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(Received 31 January 1966 and in revised form 26 September 1966)

The crystal structures of LaSi, NdSi, GdSi, HoSi, and ErSi were redetermined by means of single-crystal X-ray diffraction data. The rare earth monatomic structures crystallizing with the FeB and CrB type structures are compared with similar crystallizations found for transition metal compounds and a valence electron transfer is postulated to account for the CrB-type structures.

The silicides of the rare earths with compositions MSI have been investigated by Gladyshevskii & Kripyakevich (1964), and by Hohnke & Parthé (1966). These authors report cell constants and established from the X-ray powder patterns that the compounds have either the CrB or the FeB structure. A good discussion of the structural similarities between the FeB-type and CrB-type structures is given by Schubert (1964) and by Hohnke & Parthé (1966). Hohnke & Parthé report that DySi, HoSi and ErSi display both types of structure, while Gladyshevskii & Kripyakevich find the FeB type for DySi and HoSi and the CrB-type structure for ErSi. The FeB-type structure is exhibited also by the monosilicides between LaSi and ErSi, except EuSi which has the CrB-type structure. The CrB-type structure exists for the monosilicides between DySi and LuSi and in YSi and ScSi. The monosilicides of the rare earth elements prepared in our laboratory confirm in general the results of these authors. However, the method of preparation of these alloys employed by us produced only the CrB-type structure for HoSi and ErSi. We undertook to study these phases by means of single-crystal X-ray diffraction techniques in the hope that precise positional parameters and bond distances would lead to an understanding of the crystallizations found in these systems. At the time this study was in progress, Dr. Parthé informed us of his extensive investigation on AB compounds displaying the FeB-type and CrB-type structures and we are indebted to him for providing us with a copy of the manuscript shortly before its publication.

Rare-earth elements of commercially available purity (99.9%) and silicon (semiconductor grade, 99.9%+) in stoichiometric amounts were melted on a water-cooled copper hearth of an arc furnace in an argon atmosphere. There was negligible loss of material during melting and, therefore, the desired composition was assumed to be present in the alloys. Single crystals of LaSi of size $0.024 \times 0.037 \times 0.073$ mm and ErSi of size $0.049 \times 0.073 \times 0.122$ mm were obtained easily by breaking the samples and crushing. Powder patterns,

using a diffractometer and single-crystal oscillation, Weissenberg and precession photographs, were taken with copper or molybdenum radiation. The intensities of the various reflections were estimated visually by comparison with a prepared intensity scale and corrected for the Lorentz-polarization factor. No absorption correction was applied. The atomic parameters were refined by a full-matrix, least-squares procedure applying a weighting factor of $1/F_{\text{obs}}$ to the structure factors. The values for the atomic scattering factors were taken from *International Tables for X-ray Crystallography*. The lattice parameters reported in Table 1 were calculated from the powder patterns by minimizing the differences between $\sin^2\theta$ observed and $\sin^2\theta$ calculated to less than 0.005 and are accurate to ± 0.01 Å. The interatomic distances calculated with the use of these lattice parameters are accurate to ± 0.01 Å.

Structures of LaSi, NdSi and GdSi

The powder patterns of all these compounds were similar and Table 1 contains the lattice constants. The single-crystal photographs of LaSi showed the symmetry to be orthorhombic and the following extinctions were found: $0kl$, $k+l=2n+1$, $hk0$, $h=2n+1$, leading to the diffraction symbol $mmmPn-a$. The volume of the unit cell, 201.4 Å³, and the measured density, 5.38 g.cm⁻³, permit the placement of 4 formula weights of LaSi in the unit cell. The lattice parameters, the number of atoms in the unit cell and the space group are consistent with the FeB-type structure. The La and Si atoms were placed in the special position $4(c)$, $x, \frac{1}{2}, z$ of the centrosymmetric space group $Pnma$. The intensities of 20 $hk0$ reflections and 34 $hk1$ reflections obtained from Weissenberg photographs with Cu $K\alpha$ radiation and 22 $0kl$ reflections and 52 $h0l$ reflections obtained from precession photographs with Mo $K\alpha$ radiation were used in the structure determination. The initial x and z parameters were obtained from the $h0l$ Patterson map. The final parameters obtained from the least-squares refinement are listed in Table 2. The discrepancy coefficient is 0.134. The observed and calculated structure factors for LaSi are listed in Table 3.

* Research sponsored by National Science Foundation Grant GP-2029 and by Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, Grant 806-65.

Table 1. Lattice parameters and room temperature thermoelectric coefficients of the rare-earth monosilicides

Phase	Lattice constants	This work	Hohnke & Parthé	Gladyshevskii & Kripyakevich	Unit cell volume	Room temperature thermoelectric coefficient
LaSi (FeB)	<i>a</i>	8.38 Å	8.404 Å	8.48 Å	201.4 Å ³	-7 μV.°K ⁻¹
	<i>b</i>	3.99	4.010	4.02		
	<i>c</i>	6.02	6.059	6.04		
NdSi (FeB)	<i>a</i>	8.12	8.156	8.21	186.4	-5.5
	<i>b</i>	3.91	3.920	3.93		
	<i>c</i>	5.88	5.881	5.89		
GdSi (FeB)	<i>a</i>	7.94	7.996	8.00	175.4	-4.4
	<i>b</i>	3.86	3.859	3.85		
	<i>c</i>	5.73	5.724	5.73		
HoSi (FeB)	<i>a</i>		7.808	7.81	167.2	
	<i>b</i>		3.801	3.79		
	<i>c</i>		5.633	5.63		
ErSi (FeB)	<i>a</i>		7.772		164.7	
	<i>b</i>		3.785			
	<i>c</i>		5.599			
HoSi (CrB)	<i>a</i>	4.21	4.228		166.5	-5.5
	<i>b</i>	10.42	10.429			
	<i>c</i>	3.80	3.801			
ErSi (CrB)	<i>a</i>	4.19	4.197	4.19	163.8	-6.3
	<i>b</i>	10.35	10.382	10.40		
	<i>c</i>	3.78	3.791	3.79		

Table 2. Positional and isotropic temperature parameters for LaSi (FeB type) and ErSi (CrB type)

	<i>x</i>	$\sigma(x)$	<i>y</i>	$\sigma(y)$	<i>z</i>	$\sigma(z)$	<i>B</i>	$\sigma(B)$	Reference
La	0.1801	±0.0006	0.25		0.1136	±0.0007	-0.063	±0.13	Hohnke & Parthé (1966)
	0.178	±0.001	0.25		0.119	±0.001	1.4		
Si	0.0303	±0.0035	0.25		0.6087	±0.004	0.32	±0.43	Hohnke & Parthé (1966)
	0.032	±0.01	0.25		0.611	±0.01	1.4		
Er	0		0.1401 ± 0.0004		0.25		-0.32	±0.15	
Si	0		0.4326 ± 0.0035		0.25		0.44	±0.58	

Table 3. Observed and calculated structure factors for LaSi

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
2	0	0	96	-89	5	0	5	98	-79	10	1	0	94	88
6	0	0	120	143	8	0	5	71	66	6	2	0	62	75
8	0	0	134	-119	0	0	6	56	-65	6	2	0	97	-129
1	0	1	42	31	0	1	0	69	107	8	2	0	91	111
3	0	1	94	-80	5	0	6	45	-48	2	2	0	124	120
4	0	1	141	-161	6	0	6	57	-44	4	2	0	97	-114
4	0	1	112	126	7	0	6	126	110	6	2	0	73	80
5	0	1	89	83	8	0	6	48	39	8	2	0	54	59
6	0	1	39	-30	2	0	7	80	77	2	4	0	78	-58
9	0	1	71	-63	3	0	7	42	-31	6	4	0	89	104
10	0	1	85	81	4	0	7	121	-115	2	5	0	56	-80
11	0	1	105	86	6	0	7	32	33	1	1	1	122	-127
0	0	2	39	-36	0	0	8	100	100	2	1	1	97	101
1	0	2	164	-179	1	0	8	53	53	3	1	1	57	48
3	0	2	58	54	2	0	8	44	-45	4	1	1	50	35
5	0	2	71	65	0	1	1	107	-102	5	1	1	94	87
7	0	2	164	-156	0	1	3	116	-110	5	1	1	79	-75
9	0	2	76	60	0	1	5	52	49	7	1	1	84	-82
1	0	3	39	-23	0	1	7	91	30	8	1	1	71	77
2	0	3	96	-97	0	2	0	189	-207	1	2	1	38	-28
3	0	3	99	96	0	2	2	41	-29	2	2	1	71	75
4	0	3	122	144	0	2	4	141	158	3	2	1	120	125
5	0	3	58	-55	0	2	6	52	61	4	2	1	105	-109
6	0	3	94	-34	0	2	8	117	-95	5	2	1	68	-75
9	0	3	51	43	0	3	1	72	77	1	3	1	125	94
10	0	3	102	100	0	3	3	89	90	2	3	1	107	-75
11	0	3	90	-58	0	3	5	50	-43	3	3	1	50	-37
0	0	4	140	-176	0	3	7	89	-93	4	3	1	41	-27
1	0	4	48	-41	0	4	4	155	149	5	3	1	79	-71
2	0	4	69	67	0	4	4	122	-125	6	3	1	61	64
6	0	4	136	-118	0	4	6	49	-50	7	3	1	84	76
7	0	4	53	-46	0	4	6	61	-60	8	3	1	56	-68
8	0	4	105	102	0	5	3	68	-73	2	4	1	102	-56
1	0	5	35	-28	2	1	0	116	-168	3	4	1	124	-162
3	0	5	42	41	4	1	0	126	142	4	4	1	94	-84
3	0	5	126	128	6	1	0	87	-96	5	4	1	88	61
4	0	5	63	-57	8	1	0	67	-69	1	5	1	65	-71

The interatomic distances for near neighbors are: La-La, 3.80 (4), 3.87 Å (2) and 4.50 Å (2), Si-Si, 2.64 Å (2) and La-Si, 3.14 Å (2), 3.22 Å (1), 3.24 Å (1), 3.29 Å (1) and 3.30 Å (2).

Structures of HoSi and ErSi

The powder patterns of both compounds were similar and hence they possess the same structure. The lattice parameters of these compounds are listed in Table 1. The single-crystal photographs of ErSi proved the symmetry to be orthorhombic and the observed extinctions were: hkl , $h+k=2n+1$ and $h0l$, $l=2n+1$, consistent with the diffraction symbol $mmmC-c$. The volume of the unit cell, 164 Å³, and the measured density, 7.73 g.cm⁻³, permit the placement of 4 formula weights per unit cell. The lattice parameters, the number of atoms in the unit cell and the space group point towards a CrB-type structure. The centrosymmetric space group, $Cmcm$, was chosen and the atoms were placed in special position 4(c) 0, y , $\frac{1}{2}$. The initial y parameters were chosen from the structure of CeNi (Finney & Rosenzweig, 1961). The intensities of 29 $hk0$ reflections from precession photographs obtained with Mo $K\alpha$ radiation, 23 $0kl$ reflections and 14 $1kl$ reflections from Weissenberg photographs obtained with Cu $K\alpha$ radiation were used in the structure determination. The final

parameters are shown in Table 2. A discrepancy coefficient of 0.106 was obtained. The observed and calculated structure factors for ErSi are shown in Table 4.

The interatomic distances for near neighbors are: Er-Er, 3.46 Å (2) and 3.63 Å (4), Si-Si, 2.35 Å (2) and Er-Si, 2.92 Å (4), 3.00 Å (2) and 3.03 Å (1).

Discussion

All compounds had a metallic appearance and their measured room temperature thermoelectric coefficients (Table 1) are consistent with metallic behavior. The metallic character is also supported by the observed bond distances.

The apparent radius of silicon varies from 1.18 Å in ErSi to 1.32 Å in LaSi as compared with 1.375 Å for the radius in elementary silicon. The silicon atoms are thus found to undergo considerable contraction in the CrB-type rare-earth monosilicides. In general it is found that the silicon atoms contract in the CrB-type phases. However, the shortest Si-Si distances are found in the FeB-type monosilicides of the group IV transition elements. Thus the Si-Si bond length is 2.27 Å in ZrSi (Schachner, Nowotny & Kudielka, 1954) and 2.17 Å in TiSi (Brukl, Nowotny, Schob & Benesovsky, 1961). The transition elements undergo a small dilation in the FeB-type phases and a small contraction in the CrB-type monosilicides of the group II elements.

The monatomic rare-earth compounds with nickel (Dwight, Conner & Downey, 1965) also crystallize with the CrB and FeB-type structures. However, the structure sequence is different. Compounds between LaNi and GdNi have the CrB-type structure; those between DyNi and LuNi possess the FeB-type structure; YNi has a distorted FeB-type and ZrNi has the CrB-type structure. The structure sequences assume the following forms as the CrB and the FeB-type compounds of the transition elements are considered:

LaRh to NdRh(CrB)

LaPt, CePt(CrB)-PrPt to LuPt (excepting PmPt, EuPt and YbPt), YPt(FeB)-ZrPt, HfPt(CrB)

LaNi to GdNi(CrB)-DyNi to LuNi(FeB), YNi(FeB-distorted)-ZrNi, HfNi(CrB)

YAl, ZrAl, HfAl(CrB)

TiB(FeB)-VB, NbB, TaB, CrB, MoB(h), WB(h)-(CrB)-MoB, WB(r)(MoB)-MnB, FeB, CoB(FeB)-NiB(CrB)

ScGa, YGa, R.E.Ga(CrB)-ZrGa(MoB)

CaSi, SrSi, ScSi(CrB)-LaSi to ErSi(FeB)-DySi to LuSi, YSi(CrB)-Zr(Al, Si)(CrB)-ZrSi(CrB, FeB)-HfSi, TiSi(FeB)

CaGe, SrGe, ScGe(CrB)-LaGe, CeGe(FeB)-PrGe to ErGe, YGe (CrB)-Zr(Ga,Ge)(CrB)-(Raman & Schubert, 1965) ZrGe(FeB) (Rossteutscher & Schubert, 1965)

CaSn(CrB)

Complete literature references for the various phases mentioned in the sequences can be found in the papers by Schob & Parthé (1965), and Hohnke & Parthé (1966).

Considering the compounds with the non-transition elements, it has been pointed out (Schob, Nowotny & Benesovsky, 1961) that the FeB-type structures have a higher valence electron to atom ratio than the CrB-type structures. However, the unfilled 4*f*-transition shell seems also to influence the crystallization and to lead to cyclic repetition of structures (as shown in the structure sequences) similar to the one pointed out by Schubert (1964) for the monoborides having the FeB-type and CrB-type structures. It is found in general that the monatomic compounds of the Ce-subgroup rare earths crystallize in the same structure as the monatomic compounds of the group IV transition elements. In some specific cases as with Pt and Ge only the La and Ce compounds have the same structure as the group IV compounds. One can hence postulate that there exist similar electronic configurations or electronic interactions in the compounds of the above mentioned groups. It is improbable that the 4*f*-electrons take part in the bonding so that it appears that electron transfer from the other component occurs into the 5*d* shell of the Ce-subgroup elements in cases where the structure is the same as found in the group IV compounds. This would make the Ce-subgroup elements equivalent to the group IV transition elements in these compounds; the crystallizations of the Ce-subgroup monosilicides with the same structure as the compounds containing group IV transition elements can be explained in this manner.

It is known that the same structures occur in the compounds of group II to VII transition elements with elements lying on either side of the Cu group. For example, the following different structure types can be cited: *A*-1 and its superstructures: CuAu, Cu₃Au, TiAl₃; *A*3 and its superstructures: Ni₃Sn and TiNi₃; intermediate structures such as σ , *R*, μ , Cr₃Si, CuAl₂, Laves phases *etc.* Relevant examples of compounds crystallizing in the various structures are shown in Table 5.

The structure sequences and the occurrence of the same structures on either side of the Cu group suggest that in the compounds of the transition elements of groups II to VII with the Fe, Co and Ni group elements the unpaired electrons in Fe, Co and Ni take part in bonding and the valency can be assumed to increase from Ni towards the Fe group as it does towards the

Table 4. Observed and calculated structure factors for ErSi

h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	4	195	-217	0	4	8	96	93
0	0	6	88	83	0	4	10	135	-125
0	0	8	108	107	0	5	1	75	81
0	0	10	157	-147	0	5	3	110	-138
0	0	14	146	156	0	5	7	144	158
0	1	1	122	116	1	0	2	191	-222
0	1	3	183	-213	1	0	4	143	116
0	1	5	51	-46	1	0	6	178	184
0	1	7	194	216	1	0	8	142	-131
0	1	11	182	-153	1	0	10	135	-116
0	1	13	56	52	1	0	12	119	122
0	2	0	219	252	2	0	0	278	-244
0	2	4	160	-196	2	0	4	206	186
0	2	6	93	77	2	0	6	66	-76
0	2	8	106	101	2	0	8	104	-100
0	2	10	162	-140	2	0	10	138	139
0	3	1	101	94	3	0	2	159	157
0	3	3	160	-170	3	0	4	105	-89
0	3	5	45	-40	3	0	6	151	-154
0	3	7	181	186	3	0	8	152	114
0	3	11	181	-145	3	0	10	94	103
0	4	0	161	192	4	0	0	236	183
0	4	4	163	-155	4	0	4	161	-149
0	4	6	78	69	4	0	6	161	67

Table 5. Examples of compounds of group II to VII transition elements with the elements lying on each side of the Cu-group elements having similar structures

Structure type	T-T compounds	<i>a</i>	<i>c/a</i>	T-B compounds	<i>a</i>	<i>c/a</i>
A-1 and its superstructures						
Cu ₃ Au	TiPt ₃	3.90 Å	1.00	TiZn ₃	3.932 Å	1.00
CuAu	TiRh ⁽¹⁾	4.17	0.8	TiAl	3.997	1.019
TiAl ₃	VPd ₃	3.85	1.007	VAl ₃	3.77	1.10
A-2 and its superstructures						
CsI	TiNi	2.99	1.00	TiZn ⁽²⁾	3.15	1.00
A-3 and its superstructures						
Ni ₃ Sn	MoCo ₃	5.13	0.802	LaHg ₃ ⁽³⁾	6.822	0.725
TiNi	ThPd ₃	5.86	1.678	DyAl ₃ ⁽³⁾	6.097	1.56
Intermediate structures						
σ	Ta ₃ Rh ₂	9.754	0.518	Ta ₂ Al ⁽⁴⁾	9.972	0.523
<i>R</i>	TiMn ⁽⁵⁾	11.003	1.767	Mn ₆ Si ⁽⁶⁾	10.895	1.763
μ	NbFe ⁽⁷⁾	4.926	5.441	Nb ₆ (Cu, Al) ₇ ⁽⁸⁾	5.029	5.44
Cr ₃ Si	Mo ₃ Os	4.97	1.00	Mo ₃ Ge	4.933	1.00
CuAl ₂	Zr ₂ Ni ⁽⁹⁾	6.477	0.81	Zr ₂ Si	6.612	0.80
MgCu ₂	LaNi ₂	7.26	1.00	LaAl ₂	8.18	1.00
MgZn ₂	ZrCr ₂	5.10	1.615	ZrAl ₂ ⁽¹⁰⁾	5.27	1.662

Literature references

- (1) Raman & Schubert (1964) (6) Kuzma & Gladyshevskii (1964)
 (2) Heine & Zwicker (1962) (7) Raman (1966)
 (3) Van Vucht & Buschow (1965) (8) Osterreicher, Nowotny & Kieffer (1965)
 (4) Edshammer & Holmberg (1960) (9) Kirkpatrick, Bailey & Smith (1962)
 (5) Waterstraat (1961) (10) Wilson (1959)

The literature references for the other compounds listed can be found in Hansen (1958), Pearson (1958), or Schubert (1964).

right of the Cu group for the non-transition elements. In ZrNi and in LaNi to GdNi one can expect to have similar electronic configurations where some of the valence electrons have migrated into the 3*d* band of Ni and 5*d* band of the lanthanides. This would account for the CrB-type structure of these compounds because the overall valence electron to atom ratio would be low. The occurrence of the FeB-type structure implying a higher valence electron to atom ratio, in the compounds of the heavy lanthanides, DyNi to LuNi and in YNi would imply that none or only a small fraction of the valence electrons are localized although the reason why electron transfer should not take place in these compounds is not evident.

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