

## Structure Types of Ternary Rare Earth—Transition Metal Silicides of the $\text{LnM}_x\text{Si}_{2-x}$ Type

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Ternary rare earth silicides of the  $\text{LnM}_x\text{Si}_{2-x}$  system were investigated for the composition range between  $\text{LnSi}_2$  and  $\text{LnM}_2$ . The rare earth elements studied were Pr, Nd, Dy, and Er and the transition metals were Fe, Co, Ni, and Ag. The main structures found were of the  $\text{ThSi}_2$  and  $\text{AlB}_2$  types characteristic of the disilicides. Above 33.33 at. % transition metal content in most cases Laves phases or ternary phases were observed. The structure changes and the lattice parameters are discussed and are related to the variation in the valence electron concentration and to geometrical factors.

### Introduction

Disilicides of the rare earth metals crystallize with the tetragonal  $\text{ThSi}_2$  and hexagonal  $\text{AlB}_2$ -type structure (1). In the last few years, a number of works appeared dealing with the ternary  $\text{LnM}_x\text{Si}_{2-x}$  systems related to the disilicides. The systems investigated were those in which 3d transition metals, Al, or Ge were substituted in different amounts for Si (2-7), and the structural changes occurred as a result of this substitution were determined.

The results reported in the above studies cover only small portions of the composition ranges in the  $\text{LnM}_x\text{Si}_{2-x}$  system and are related to only a few of the rare earth elements. Therefore it was decided to undertake a systematic study of this ternary system, covering the whole composition range between  $\text{LnSi}_2$  and  $\text{LnM}_2$ , with the representative rare earth elements Pr, Nd, Dy, and Er and with the transition elements Fe, Co, Ni, and monovalent Ag. The aim of this study was to determine the way in which the structural changes occurring when transition metal atoms replace Si in the rare earth disilicides depend on the valence electron concentration and geometrical factors.

### Experimental

Samples have been prepared by melting together rare earth metals, silicon, and the transition metals (Fe, Co, Ni, and Ag) all 99.9% pure.

The metals were mixed together and heated by an induction furnace at about 1600°C under the protective atmosphere of argon. Alumina crucibles were used as containers. To ensure homogenization of the samples, they were annealed by keeping them in the induction furnace somewhat lower than the heating temperature for 30 minutes. The purity of the samples was checked by the X-ray diffraction method.

Powdered samples were X-ray analyzed by a Phillips Diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation, monochromatized with graphite. The cell parameters were calculated by a least-squares program (8) using an average of 15 reflections. The maximum error in the lattice constants is 0.005 Å.

X-Ray intensities were recorded on a strip chart while scanning at 0.25° (2θ)/minute and measuring the area of the peaks. The structure factors were calculated by a computer program (9).

### Results

The  $\text{LnNi}_x\text{Si}_{2-x}$  system has been investigated for Pr, Nd, Dy, and Er. The structure type and the lattice parameters of the compounds at different compositions are listed in Table I. The structural changes observed at the different compositions can be described as follows:

At a Ni content of 12.5 at. %, all the compounds crystallize in the  $\text{ThSi}_2$ -type tetragonal structure. At a higher Ni content, the  $\text{AlB}_2$ -type



TABLE II  
RELATIVE INTEGRATED INTENSITIES OF  $\text{ThSi}_2$ -TYPE  $\text{PrNiSi}$

$hkl$	$I_{\text{obs}}$	$I_{\text{intermittent}}$	$I_{\text{random}}$
1 0 1	40.0	33.0	27.0
0 0 4	25.6	7.5	6.8
1 0 3	100	100.0	100.0
1 1 2	140	113.0	102.8
1 0 5	71.8	71.0	64.9
2 0 0	98.4	53.4	48.7
1 1 6/2 1 1	10.3	11.2	10.5
1 0 7	36.6	13.7	10.9
2 1 3	27.5	33.6	30.4
2 1 5	55.0	36.0	31.7
1 1 8	38.4	18.0	16.6
2 2 0	16.6	10.2	9.4
2 1 7	15.6	18.0	16.4
		$R = 0.29$	$R = 0.39$

hexagonal structure was obtained with limiting composition  $\text{LnNi}_{0.75}\text{Si}_{1.25}$ . The homogeneity range of the  $\text{AlB}_2$ -type hexagonal structure is apparently broader than that of the  $\text{ThSi}_2$ -type structure. At a composition of  $\text{LnNiSi}$ , the Pr and Nd compounds crystallize in the  $\text{ThSi}_2$ -type structure, while for the Dy and Er compounds the  $\text{ThCr}_2\text{Si}_2$ -type body-centered tetragonal structure was observed together with small amounts of  $\text{Dy}_2\text{O}_3$  and  $\text{Er}_2\text{O}_3$ , owing to an excess of Dy and Er during the formation of  $\text{Dy}(\text{Er})\text{Ni}_2\text{Si}_2$ .

The compounds with more than 50 at. % Ni ( $\text{LnNi}_{1.25}\text{Si}_{0.75}$  and  $\text{LnNi}_{1.5}\text{Si}_{0.5}$ ) crystallize with

a tetragonal structure in the case of Pr and Nd, and hexagonal structure in the case of Dy. We could not relate these structures to crystal phases known for silicides or other intermetallic compounds. In the composition range of 75–100 at. % Ni the main structure type is of the cubic  $\text{MgCu}_2$  phase except for  $\text{PrNi}_{1.75}\text{Si}_{0.25}$ , which crystallizes in the  $\text{MgZn}_2$ -type structure.

In order to determine the exact position of the Ni and Si atoms in the  $\text{ThSi}_2$ -type  $\text{Pr}(\text{Nd})\text{NiSi}$  compounds, X-ray intensity measurements were carried out for  $\text{PrNiSi}$ . The structure factors were calculated for two cases; in one case Ni and Si atoms were randomly distributed between the Si sites of the  $\text{ThSi}_2$  structure and in the second case Ni and Si atoms were intermittently distributed between these two positions. Results of the intensity calculations are given in Table II. It can be concluded from this table that agreement between observed intensities and calculated intensities is better when Ni and Si are intermittently located forming Ni–Si–Ni–Si– chains, the interchain bond always being between Ni and Si atoms.

To study the replacement of Si by different transition metals, the  $\text{NdM}_x\text{Si}_{2-x}$  system was investigated for Fe, Co, and Ag. The results obtained for the  $\text{NdFe}(\text{Co})_x\text{Si}_{2-x}$  system are summarized in Table III. In contrast to the results with Ni, the  $\text{AlB}_2$  structure in the compounds with Fe and Co was obtained only at a critical composition of  $\text{NdFe}(\text{Co})_{0.4}\text{Si}_{1.6}$ . In the case of the Co compound, the stability range of the structure was somewhat broader, but at the composition of  $\text{NdCo}_{0.67}\text{Si}_{1.33}$ , the  $\text{ThCr}_2\text{Si}_2$

TABLE III  
CRYSTAL DATA OF THE  $\text{NdFe}(\text{Co})_x\text{Si}_{2-x}$  SYSTEM

M		Fe		Co		
Composition	Structure type	$a$ (Å)	$c$ (Å)	Structure type	$a$ (Å)	$c$ (Å)
$\text{NdM}_{0.25}\text{Si}_{1.75}$	$\text{ThSi}_2$	4.115	13.90	$\text{ThSi}_2 + \text{AlB}_2$	4.168	13.74
$\text{NdM}_{0.4}\text{Si}_{1.6}$	$\text{AlB}_2$	4.031	4.192	$\text{AlB}_2$	4.029	4.211
$\text{NdM}_{0.67}\text{Si}_{1.33}$	—	—	—	$\text{AlB}_2 + \text{ThCr}_2\text{Si}_2$	4.039	4.199
$\text{NdM}_{0.75}\text{Si}_{1.25}$	—	—	—	$\text{AlB}_2 + \text{ThCr}_2\text{Si}_2$	4.054	4.169
$\text{NdMSi}$	$\text{TiNiSi}$	$\frac{a}{11.18} \frac{b}{6.89}$	5.32	$\text{PbFCl}$	4.035	6.895
$\text{NdM}_{1.25-1.5}\text{Si}_{0.75-0.5}$	—	—	—	$\text{ThCr}_2\text{Si}_2$	3.954	9.911
$\text{NdM}_{1.75}\text{Si}_{0.25}$	—	—	—	—	—	—
$\text{NdM}_2$	—	—	—	$\text{MgCu}_2$	7.428	—
				$\text{MgCu}_2$	7.283	—

TABLE IV  
CRYSTAL DATA FOR THE NdAg<sub>x</sub>Si<sub>2-x</sub> SYSTEM

<i>x</i>	Structure type	VEC	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>
0.00	GdSi <sub>2</sub>	3.666	4.18, 4.15	13.56	3.256
0.20	ThSi <sub>2</sub>	3.466	4.166	14.10	3.385
0.33	ThSi <sub>2</sub>	3.333	4.172	14.22	3.408
0.50	ThSi <sub>2</sub>	3.166	4.175	14.31	3.428
0.66	ThSi <sub>2</sub>	3.000	4.184	14.50	3.465
0.75	ThSi <sub>2</sub>	2.916	4.188	14.70	3.510
1.00	AlB <sub>2</sub>	2.666	4.244	4.138	0.975
1.25	AlB <sub>2</sub>	2.416	4.295	4.135	0.963

phase appeared together with the AlB<sub>2</sub> structure. In the case of NdFeSi, an orthorhombic structure of the TiNiSi type was obtained with some FeSi impurities. The same structure was obtained also for PrFeSi, with lattice constants  $a = 11.13$ ,  $b = 7.04$ , and  $c = 5.30$  Å. In the case of NdCoSi, two types of tetragonal phases were observed, the PbFCI and the ThCr<sub>2</sub>Si<sub>2</sub>-type structure. NdCo<sub>2</sub> was found to crystallize with the MgCu<sub>2</sub> structure. NdFe<sub>2</sub> could not be prepared.

In Table IV, results obtained in the NdAg<sub>x</sub>Si<sub>2-x</sub> system are listed. The stability range of the ThSi<sub>2</sub>-type structure is much broader than in the case of Fe, Co, and Ni. The AlB<sub>2</sub> structure was observed only at a composition of NdAgSi. In the case of the ThSi<sub>2</sub>-type compounds the lattice constants and the  $c/a$  value increase with the Ag content. The composition range of the ThSi<sub>2</sub>- and AlB<sub>2</sub>-type structures was also determined in the case of two smaller rare earth elements, Dy and Er. In these cases, the AlB<sub>2</sub> structure appears in the composition range Dy(Er)Ag<sub>0.67</sub>Si<sub>1.33</sub>-Dy(Er)AgSi.

### Discussion

The results summarized in this work deal with the rare earth metal-transition metal-silicon system, in which the rare earth metal content has a constant value of 33.33 at. %. Up to a transition metal content of 33.33 at. %, the ThSi<sub>2</sub>- or AlB<sub>2</sub>-type structures characteristic of the binary rare earth silicides were observed. At higher transition metal content, a larger variety of structures characteristic of ternary phases or of the Laves phases appears. Another general conclusion concerning these compounds is that the Ni ternary systems are richest in distinct

phases; the number of compounds decreases toward Co and Fe. Similar results were obtained by Bodak et al. (5) in the case of the Ce-Ni-Si system.

The main difference between binary silicides and those studied in this work is because of the replacement of Si by transition metals of different radius, and the changes in the valence electron concentration (VEC) when transition metals are substituted for the tetravalent Si. The structural changes will be, therefore, explained below in terms of the above two factors.

In the ThSi<sub>2</sub>-type compounds, the VEC decreases when transition metals are inserted and at the same time  $c/a$  increases.  $c/a$  as a function of VEC is given in Fig. 1 for the NdAg<sub>x</sub>Si<sub>2-x</sub> system. The shortest Si-Si bond is defined by

$$\sqrt{a^2/4 + (0.072c)^2}$$

and is present in the Si chains of the structure. The atomic radius of Si (1.32 Å) is bigger than that of Ni (1.24 Å) (10) and, therefore, insertion of Ni in these chains will lower the parameter  $a$ . Similar observations were made when Ge was substituted for Si in rare earth disilicides (7). The value of  $c$ , on the other hand, depends on the rather long Si-Si interchain bonds (Si-Si = 0.178*c*). These bonds become weaker when Ni is substituted for Si and the VEC decreases. The weaker interchain bonds will be longer and consequently  $c$  increases. The relatively large interchain bonds are not affected by the size of Ni but by its VEC; this also is consistent with that found in the Ln-Ge-Si system, where insertion of isoelectronic Ge for Si does not influence  $c$ .

Two extreme cases for the composition range of stability of the AlB<sub>2</sub> structure were found:

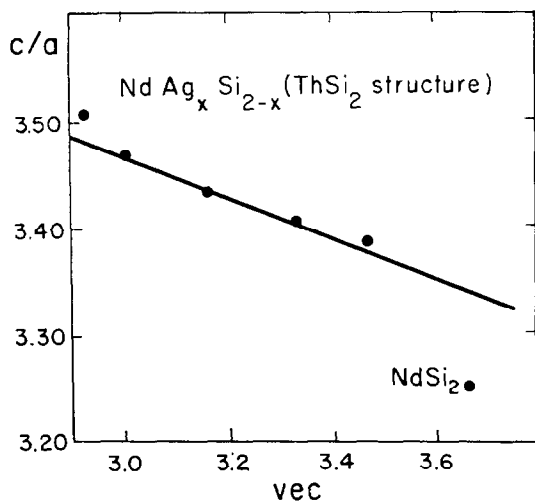


FIG. 1.  $c/a$  versus VEC in the  $\text{ThSi}_2$ -type  $\text{NdAg}_x\text{Si}_{2-x}$  system.

$\text{LnCu}_{1.5}\text{Si}_{0.5}$  (11) and the critical composition of  $\text{LnFe}_{0.4}\text{Si}_{1.6}$ . The critical composition mentioned corresponds to a VEC value of 3.4, critical to obtain the  $\text{AlB}_2$  structure, which, as a rule, appears always at lower VEC than the  $\text{ThSi}_2$ -type structure (12). This composition is also required to have at least one transition metal in each of the Si hexagons characteristic of the  $\text{AlB}_2$ -type structure. Generally, the homogeneity range of the structure increases in the order of  $\text{Fe} < \text{Co} < \text{Ni} < \text{Cu}$ . The transition metal atoms replace the silicon in their sites (2), and, therefore, the radius of the Si atoms calculated in the ternary compounds gives the mean value of these radii. In the  $\text{NdM}_{0.4}\text{Si}_{1.6}$  system, these radii were found to be 1.117, 1.122, 1.131, and 1.133 Å for  $\text{M} = \text{Fe}, \text{Co}, \text{Ni},$  and  $\text{Cu}$ ,<sup>1</sup> respectively. Accordingly, the size of the transition metals in these compounds will be  $\text{Fe} < \text{Co} < \text{Ni} < \text{Cu}$ . This means that the size of the transition metals and the homogeneity range of the  $\text{AlB}_2$  structure increases in the same order, indicating that substitution of Si by one of the above atoms will be most favorable with atoms similar in size to Si.

Increase in the Ni content of the  $\text{LnNi}_x\text{Si}_{2-x}$  compounds with the  $\text{AlB}_2$  structure caused an increase in the parameter  $a$  and a decrease in  $c/a$ . The value of  $a$  depends on the length of the Si-Si bond (Si-Si is, by a good approximation,  $a/\sqrt{3}$ ). The insertion of Ni in the  $\text{AlB}_2$ -type structure affects the bond in a different way than in the  $\text{ThSi}_2$ -type structure, where the Si-Si

<sup>1</sup> Calculated from the data for  $\text{NdCu}_{0.5}\text{Si}_{1.5}$  (11).

bonds are relatively longer; namely, it will weaken these bonds because of the decrease of the VEC. The bonds will become longer and  $a$  will increase. As a result of the longer Si-Si bonds, the graphitic layers become broader and this enables the rare earth metals to penetrate deeper into these layers.  $c$ , which is a measure of the distance between the metallic layers, will then decrease. At compositions above 37.5 at. % transition metal content, the  $\text{AlB}_2$  structure disappears. At this composition, at least two Si atoms are replaced by the smaller transition metal atoms, and the silicon hexagons become distorted to such an extent that the structure is destroyed and the  $\text{ThSi}_2$ -type structure reappears ( $\text{NdNiSi}$ ).

The transition  $\text{ThSi}_2 \rightarrow \text{AlB}_2$  in the case of the  $\text{LnAg}_x\text{Si}_{2-x}$  system occurs at higher Ag content than in the cases of Fe, Co, Ni, and Cu. The reason for this seems to be that the insertion of the relatively big Ag atoms reduces the effective space in the Si hexagons, which then can no longer accommodate the rare earth atoms.  $\text{ErAg}_{0.67}\text{Si}_{1.33}$  is hexagonal, because at this composition two Ag atoms have already replaced Si atoms in the hexagons, and these expand owing to their increasing Ag character. In the  $\text{NdAg}_x\text{Si}_{2-x}$  system, the  $\text{AlB}_2$  structure was obtained only at a composition of  $\text{NdAgSi}$  because more Si has to be replaced by Ag in order to make room for the larger Nd atoms.

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