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THE CHEMISTRY OF THE SILICIDES OF THE RARE-EARTH ELEMENTS

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1. INTRODUCTION

One of the most important conditions for the development of modern technology is the production of new high-temperature materials with special physical and chemical properties — semiconducting, magnetic, nuclear, refractory, emission, and high-temperature strength properties. In this connection the silicides of the rare-earth metals are attracting attention. Compounds of the rare-earth elements are also of theoretical interest, since, unlike the transition metals, in which the d levels are being filled, lanthanum and the lanthanides have incomplete inner $4f$ levels, which cannot participate directly in chemical bonding, but which can exert an influence on the nature of the chemical bond formed by the electrons in the outermost levels. In particular, since the $4f$ and $5d$ states are close to one another, the latter may arise in crystals of the compounds as a result of $f \rightarrow d$ transitions.

Because of this and the simultaneous existence, in the silicide lattices, of covalent bonds between the silicon atoms and metallic bonds between the atoms of the metals and silicon, the bonding in silicides is of complex character, and this makes it possible to vary the physical and chemical properties of these compounds over wide limits. Scandium and yttrium resemble the lanthanides extremely closely in many of their properties, their geochemical features, and their behaviour in compounds. These two elements are intermediate between the d and f transition elements; their silicides exhibit features characteristic both of the silicide phases of transition metals of Groups IV–VIII and of the silicides of the lanthanides.

The problems of the further study of the electronic structure and physical properties of the silicides of the rare-earth elements and the extension of the range of their application makes it necessary to summarise the available information on this group of inorganic compounds.

2. STRUCTURE AND PROPERTIES

The characteristic type of crystal structure shown by the disilicides of the rare-earth metals is the α-$ThSi_2$ structure, in which the silicon atoms form a three-dimensional framework (Fig.1) and the metal atoms are situated in the spaces in this framework (the unit cell contains 4 atoms). This type of structure is produced when the silicon: metal radius ratio $r_{Si} : r_M = k$ is greater than 0.7 and less than 0.8 ($0.7 < k < 0.8$). This corresponds to the silicides of almost all the rare-earth metals, since for the latter $k = 0.69_5–0.75_5$. In this case the significant difference in atomic radii does not favour the close packing of silicon and metal, as in the silicides MSi_2 of the iron disilicide type. Every silicon atom in silicides of the α-$ThSi_2$ type is surrounded by three neighbouring silicon atoms and six metal atoms. The Si–Si distances indicate the existence of covalent bonding (close to $2r_{Si} = 2.35$ Å). The configuration of the bonds corresponds to sp^3 hybridisation. On the other hand, the M–Si distances indicate the absence of covalency, or the existence of weak covalent bonds, between the atoms of metal and silicon in a structure of this type. This bond is apparently metallic in character.

The silicides of lanthanum, cerium, praseodymium, and europium have this type of structure, but the silicides of neodymium, samarium, gadolinium, dysprosium, and yttrium crystallise in a slightly different orthorhombic

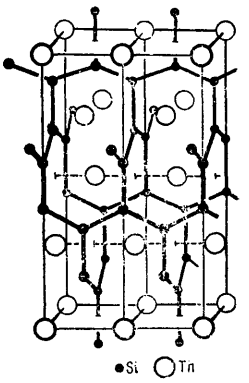


Fig. 1. The crystal structure of α-$ThSi_2$.

TABLE 1. Crystal structures of the silicides of the rare-earth elements.

Silicide	Structural type	System	Space group	Lattice constants, kX			Density, g cm^{-3}	Ref.
				a	*b*	*c*		
YSi	CaSi	orthorhombic	D_{2h}^{17}	4.25	10.52	3.826	4.53	2
Y_5Si_3	Mn_5Si_3	hexagonal	D_{6h}^{3}	8.403	—	6.303	—	4
α-YSi_2	α-YSi_2	orthorhombic	D_{2h}^{28}	4.04	3.95	13.23	4.5	3
β-YSi_2	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.04	—	13.42	—	5
$LaSi_2$	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.31	—	13.80	5.0	3
CeSi	FeB	orthorhombic	D_{2h}^{16}	—	—	—		2
$CeSi_2$	FeB	orthorhombic	D_{2h}^{16}	4.27	—	13.88	5.45	3
α-$PrSi_2$	α-YSi_2	orthorhombic	D_{2h}^{28}	4.23	4.20	13.68	—	4
β-$PrSi_2$	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.20	—	13.76	—	3
α-$NdSi_2$	α-YSi_2	orthorhombic	D_{2h}^{28}	4.18	4.15	13.56	4.7	3, 6
β-$NdSi_2$	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.03	—	13.53	5.84	1, 7
α-$SmSi_2$	α-YSi_2	orthorhombic	D_{2h}^{28}	4.105	4.035	13.46	—	3
β-$SmSi_2$	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.08	—	13.51	6.26	4
$EuSi_2$	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.29	—	13.66	—	3
α-$GdSi_2$	α-YSi_2	orthorhombic	D_{2h}^{28}	4.09	4.01	13.44	6.4	3
β-$GdSi_2$	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.10	—	13.61	5.92	5
α-$DySi_2$	α-YSi_2	orthorhombic	D_{2h}^{28}	4.04	3.95	13.34	6.8	3
β-$DySi_2$	α-$ThSi_2$	tetragonal	D_{4h}^{19}	4.03	—	13.58	—	5

lattice (Table 1), in which, however, the *a* and *b* axes differ little from one another, so that Brauer and Haag[1,2] attributed to neodymium disilicide a tetragonal lattice analogous to the lattices of lanthanum, cerium, and praseodymium silicides. The relative positions of the metal and silicon atoms in these structures are the same as those in the α-$ThSi_2$ structure. The transition from tetragonal to orthorhombic lattice at room temperature in the series of disilicides of the rare-earth metals La, Ce, Pr, Nd, ..., the increase in the degree of "orthorhombic character" of the lattice in the series $NdSi_2$, $SmSi_2$, $GdSi_2$, $DySi_2$, *i.e.* the difference between the constants *a* and *b* (0.03 Å, 0.07 Å, 0.08 Å, and 0.09 Å respectively), and the reappearance of a tetragonal lattice in $EuSi_2$ and its subsequent replacement by an orthorhombic lattice in $GdSi_2$ can, according to Perri *et al.*[3], be attributed to the effect of the lanthanide contraction. The lattice constants of the disilicides of the rare-earth metals show the same dependence on atomic number as those of the rare-earth metals themselves and their borides, *i.e.* a continuous decrease from $LaSi_2$ to $DySi_2$ (and apparently further, to the end of the lanthanide series), with a sharp increase at $EuSi_2$ (Fig. 2) and, apparently, at $YbSi_2$. A change of this type for metallic Eu and Yb is related to the attraction of an electron from the outer $5d^1$ orbital to fill the vacant state (hole) in the inner $4f^6$ orbital[3].

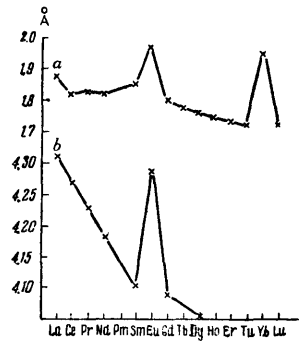


Fig. 2. Dependence of the atomic radii of the rare-earth metals (*a*) and the lattice constants of their silicides (*b*) on the atomic number of the elements.

According to Perri *et al.*[5], the lattice of the disilicides of Sm, Gd, Dy, and Y, which is orthorhombic at room temperature, changes above 300°–500° to a tetragonal modification of the α-$ThSi_2$ type, analogous to that of $LaSi_2$ and $CeSi_2$. In the case of $PrSi_2$ the orthorhombic α modification exists only below -120°. The orthorhombic $\rightleftharpoons$ tetragonal transformation temperature increases with increase in the atomic number of the metal. No orthorhombic modification of $EuSi_2$ has been found (Table 1).

The monosilicides of rare-earth metals, known at present for yttrium, lanthanum, and cerium, crystallise in lattices of the orthorhombic-bipyramidal system. Analysis of the silicon : metal radius ratio at which the orthorhombic monosilicides are formed shows that they are produced when the difference in atomic radii is large (k = 0.6–0.9). These complex structures are distinguished by the presence of a chain of covalent bonds between the silicon atoms. The tendency for the structure to become more complex and for covalent bonds to be produced between the silicon atoms as the value of k departs from unity is a general feature of all compounds of transition metals with silicon[8]. However, a marked difference in the radii of the atoms of metal and silicon is not the only condition for the production of orthorhombic lattices in monosilicides of the transition metals and, more particularly, rare-earth metals; a second necessary condition is a certain effective electron concentration, which can be characterised by the ratio Z/ζ†, since the effective electron concentration in the lattice is greater, the greater the total number of valency

† Z is the sum of the number of valency electrons of the metal and silicon, and $\zeta = 1/Nn$, where N is the principal quantum number of the unfilled level and n the number of electrons in this level[9].

electrons of the metal and silicon, and smaller, the greater the acceptor power of the unfilled sub-levels in the atom of the transition metal. Fig.3 [10] shows that the k *vs.* Z/ζ diagram is divided into three regions, the upper and lower corresponding to the orthorhombic monosilicides, and the central to the cubic monosilicides. It follows from this diagram that the orthorhombic monosilicides are formed either when there is a considerable difference in the atomic radii of the metal and silicon, irrespective of the electron concentration, or, in the case where the atomic radii of the metal and silicon are similar, when there is a high electron concentration, requiring a more capacious Brillouin zone. The first case is also characteristic of yttrium and cerium monosilicides.

Examination of the known melting points of disilicides of the rare-earth metals (Table 2) shows that the ratio of these melting points, on the absolute scale, to the melting points both of the metals and of silicon is greater than unity, but as a rule, unlike the case of the borides, it is not much greater than 1. In general, the ratio $T_{M_xSi_y} : T_M$ decreases with increase in the silicon content of the silicide phase. This indicates a weakening of the bonds between the metal atoms in the silicide lattices and is in good agreement with the increase, in the same direction, of the silicon motif in the structure. In this case the $T_{M_xSi_y} : T_M$ ratio also decreases, approaching unity for compounds with the greatest number of Si–Si bonds, *i.e.* those in which the silicon motif is shown to the greatest extent.

This is well illustrated, in particular, by the silicides of rare-earth elements exhibiting a three-dimensional framework of Si–Si bonds (Table 2).

Another noteworthy feature is that for silicides with an orthorhombic lattice (yttrium, gadolinium, and dysprosium disilicides), the ratio of the melting points to the melting points of the corresponding metals is much less than in the case of the disilicides with the tetragonal lattice.

There are almost no data on the heats of formation of the silicides. Brewer and Krikorian [11] estimated the heat of formation of cerium silicide $CeSi_2$ and obtained values in the range 16.6–34.4 kcal per atom of Si (the recommended mean value is 25 ± 10 kcal per atom of Si), or about 50 kcal mole^{-1}. Neshpor [10], on the basis of an analysis of the manometric curves for the preparation of lanthanum mono- and di-silicides *in vacuo* by reduction of lanthanum oxide with silicon, obtained approximate values for the heats of formation of LaSi (30 kcal mole^{-1}) and $LaSi_2$ (44.4 kcal × mole^{-1}). From this, the heat of formation of lanthanum disilicide is ~ 22 kcal per atom of Si, which is close to the corresponding value for cerium disilicide (25 kcal per atom of Si), found by Brewer and Krikorian. The heat of formation of yttrium monosilicide YSi is 32.2 kcal mole^{-1}. [12]

TABLE 2. Melting points of the disilicides of the rare-earth metals.

Silicide	Melting point, °C	$T_{M_xSi_y} : T_M$	$T_{M_xSi_y} : T_{Si}$
YSi_2	1520	1.04	1.04
$LaSi_2$	1520	1.50	1.04
$NdSi_2$	1525	1.39	1.05
$EuSi_2$	1500	1.39	1.03
$GdSi_2$	1540	1.12	1.06
$DySi_2$	1550	1.03	1.06

The electrical conductivity, Seebeck coefficient, and Hall effect have been studied for only a few disilicides [13–16]. The results are given in Table 3, which also gives for comparison the data for the corresponding metals.

The resistivity of the disilicides of the rare-earth metals (Table 3) is considerably greater than that of the corresponding metals and is ~10^{-4} Ω cm, but is considerably less than that of semiconducting silicides such as $CrSi_2$ and $ReSi_2$. [15] The silicides of the rare-earth metals, like the metals themselves, have low Seebeck coefficients. The same is true of the values of the Hall coefficients. In the case of praseodymium disilicide, however, the sign of the Hall effect is the opposite of that for the metal, and this may indicate a significant difference in the nature of the energy spectrum of the electrons in praseodymium and its silicide.

The temperature dependence of the resistance and Seebeck coefficient has been studied for lanthanum disilicide [13,14]. The resistance of $LaSi_2$ (Fig.4) has an anomalous temperature dependence — almost linear, like that characteristic of metallic conductors, and showing an increase with increase in temperature to ~500°, followed by a fairly sharp decrease and changing to a smoother curve with further increase in temperature. The anomalous temperature dependence of the resistance of $LaSi_2$ may be caused either by a change in the mechanism of conductance due to an increase in the La–La distance as a result

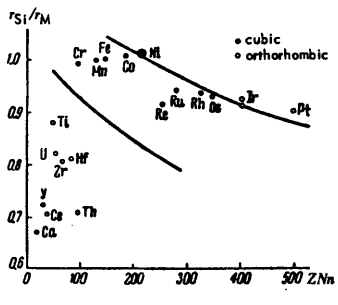


Fig.3. Dependence of the nature of the structure of silicides of transition elements on the ratio $r_{Si} : r_M$ and the product ZNn. [15]

TABLE 3. Electrophysical properties of the disilicides of the rare-earth metals [13–16].

Silicide or metal	Electrical resistivity, μΩ cm	Hall coefficient, $10^8 R$, cm^3 C^{-1}	Absolute Seebeck coefficient, μV deg^{-1}
La	56.8	−8.0	—
$LaSi_2$	236±20	−17.5±0.4	−4.2±0.3
Ce	75.3	+18.1	—
$CeSi_2$	408±20	+19.3±1.0	+7.8±0.5
Pr	68.0	+7.1	—
$PrSi_2$	202±20	−10.7±0.5	−3.2±0.4
$NdSi_2$	349	—	—
$GdSi_2$	263	—	—
$DySi_2$	3020	—	—

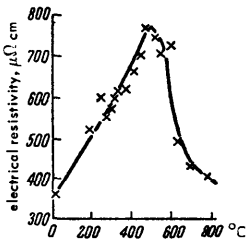


Fig.4. Temperature dependence of the electrical resistivity of $LaSi_2$. [12]

of thermal expansion or by a polymorphic transformation. The latter has been established for $ThSi_2$,[17] whose low-temperature modification is isostructural with $LaSi_2$. Microstructural studies, however, have shown no changes on passing through 500°.

The absolute Seebeck coefficient of lanthanum silicide (Fig. 5) is negative throughout the whole temperature range studied, indicating that the current carriers have negative sign, and passes through a minimum at 500°–600°. At ~500° the curve giving the temperature dependence of the Seebeck coefficient changes sign, like that giving the temperature dependence of the resistance. The Hall constant for $LaSi_2$ at room temperature is negative and has the value -17.5×10^{-5} cm^3 C^{-1}.

Analysis of the temperature dependence of the resistance of lanthanum silicide in the non-linear region shows that it is given by the exponential $\rho_t = \rho_0 \exp(0.19/kT)$, *i.e.* it does not obey either the T^3 (or T^5) law required by theory for $T = \theta$, where θ is the Debye temperature, equal to 502°K for $LaSi_2$, or the $T^{3/2}$ law required by theory for semiconductors with high conductivity[18]. Calculation of the resistance of lanthanum disilicide from Grüneisen's formula[19] for metals does not give satisfactory agreement with experimental data either:

Temperature, °C	0	100	200	300	400	500
Reduced resistivity:						
calculated	0.48	0.71	0.93	0.16	1.37	1.59
experimental	0.67	0.81	0.95	1.10	1.25	1.43

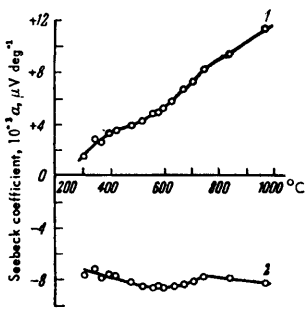


Fig.5. Temperature dependence of the Seebeck coefficient of $LaSi_2$. [12]

All this indicates that the nature of the conductivity in metallic silicides, to which class $LaSi_2$ belongs, is more complex than that for metals. In any case it may be assumed that $LaSi_2$ is a metallic conductor of the n-type from 20° to 500° and a semiconductor, apparently of the p-type, above 500°.[13]

The width of the forbidden gap in the region corresponding to the semiconductor temperature dependence of the conductivity of $LaSi_2$ is ~0.19 eV. This behaviour of lanthanum disilicide cannot be explained by the theory of semiconductors with an impurity zone[6], since it is then difficult to explain the whole course of the temperature dependence of the resistivity of $LaSi_2$ in the region where it is increasing, and also since the width of the forbidden gap in the region of the semiconductor temperature dependence of the resistivity is too small. It may, however, be suggested that the observed nature of the temperature dependence of the resistivity of $LaSi_2$ is related to the anisotropy of its thermal expansion. The latter, as a result of the markedly heterodesmic nature of the interatomic bonds in the lattice of this compound, may lead to a significant change in the nature of the overlap of the energy bands in the valency zone, which at low temperatures is also the conductivity zone. Taking into consideration the electronic structure of semiconducting silicides[19], we may assume that the single *d* electron in lanthanum is used for bonding between silicon atoms at high temperatures. This effect leads to the filling of a band of electronic states, whose production is due to the participation of the silicon atoms in the chemical bonding and to the appearance of an energy gap between this filled band and higher free bands. It is evident that the appearance of a gap between the conducting and non-conducting states in a certain temperature range should lead first to a considerable increase in resistance with increase in temperature and then to its exponential decrease. The low Hall mobility of the current carriers in $LaSi_2$ (Table 4) indicates that the electrons in $LaSi_2$ are bound to a considerable extent, so that even a slight redistribution of electrons may lead to a change in the nature of the conductivity.

Preliminary study of the temperature dependence of the electrical resistance of $CeSi_2$ [13] has revealed its semiconductor character throughout the whole temperature range 20°–1000°.

There are very few data on the magnetic properties of the silicides of the rare-earth metals. Matthias *et al.*[20] observed ferromagnetism in praseodymium disilicide at very low temperatures, its Curie point lying at 10.5°K, but the silicides of Sc, Y, La, Ce, and Nd were found to be paramagnetic down to ~1°K.

TABLE 4. Effective concentration of free current carriers and Hall mobility of the current carriers in silicides of the rare-earth metals.

Phase	Effective concentration of free current carriers, *n*		Hall mobility of the free current carriers, cm^2 V^{-1} sec^{-1}
	per cm^3	per molecule	
$LaSi_2$	$2.9 \cdot 10^{22}$	2	0.7—(for La 1.4—)
$CeSi_2$	$3.1 \cdot 10^{22}$	2.3	0.5+(for Ce 2.4+)
$PrSi_2$	$4.4 \cdot 10^{22}$	3.4	0.5—(for Pr 0.5—)

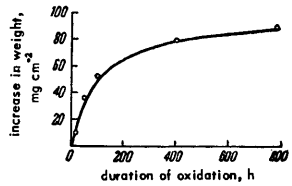


Fig.6. Change in weight of $DySi_2$ specimen during oxidation in air at 1000°. [16]

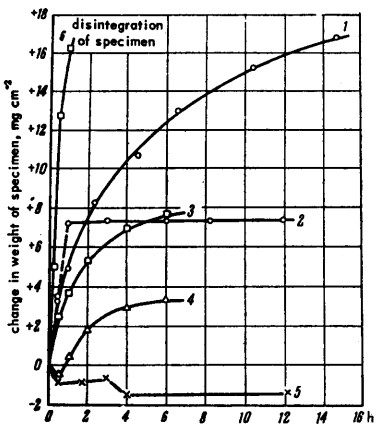


Fig.7. Change in weight during oxidation for the silicides of some transition metals at 1300°: 1) $BaSi_2$; 2) $ReSi_2$; 3) $MnSi_2$; 4) $FeSi_2$; 5) $CrSi_2$; 6) $LaSi_2$.

The hardness of the silicides of the rare-earth metals is much lower than that of the corresponding borides:

Phase	Microhardness $H_{1/2}$, kg mm⁻²	Phase	Microhardness $H_{1/2}$, kg mm⁻²
$LaSi_2$	325	LaB_6	2500
$CeSi_2$	545	CeB_6	2350

This can be attributed both to the considerable weakening of the bond between the metal atoms in the silicides and to the characteristic structural features of the latter, facilitating the shearing deformation characteristic of hardness measurements. The nature of the change in the hardness is exactly analogous to that of the change in the melting points.

Binder [21] gives the bending strength (kg mm^{-2}) of some disilicides: $LaSi_2$ 27.2, $GdSi_2$ 4.4, and $DySi_2$ 6.68.

The resistance of the silicides of the rare-earth metals to oxidation, like that of the silicides of the *d*-transition metals, depends to a marked extent on the nature of the oxide film produced, the volatility of the oxide, and the tendency of the oxide to form silicates with SiO_2. Thus according to Binder's data [21], dysprosium disilicide $DySi_2$ shows a comparatively high resistance to oxidation at 1000° and a marked decrease in the rate of oxidation with time (Fig. 6), whereas Neshpor [12] found that lanthanum disilicide is oxidised extremely rapidly (Fig. 7) with the formation of a grey non-compact oxide film which did not adhere to the specimen surface; the latter also showed considerable cracking. However, Neshpor's experiments were carried out at a higher temperature (1300°). It may be suggested that the difference in the behaviour on oxidation shown by lanthanum and dysprosium disilicides is due to a difference in the tendency to form silicates, since a marked difference in the volatility of these oxides is not to be expected.

According to Brauer and Haag [1], the disilicides of the rare-earth metals are readily decomposed by HF solutions, dilute HCl, and molten $K_2CO_3 + Na_2CO_3$, which is used in the chemical analysis of these compounds.

3. METHODS OF PREPARATION

The chief methods of preparing the silicides of the rare-earth metals are similar to the methods of preparing the borides, and can be divided into the following groups: (1) direct combination of the rare-earth metal and silicon, (2) the reduction of oxides of the rare-earth metals with silicon, and (3) the electrolysis of melts containing the rare-earth metals and silicon.

The direct combination of the rare-earth metals and silicon can be carried out by fusion or sintering. This method appears to have been used first by Vogel [22] for the preparation of cerium–silicon alloys. Brewer and Krikorian [11] used the same method to prepare these cerium–silicon alloys by sintering small pieces of cerium with silicon powder at 1430° (with partial fusion of the specimens). Because of the high affinity of the rare-earth metals for oxygen and nitrogen, the sintering or fusion with silicon should be carried out in an inert atmosphere (argon, etc.), and this makes the method complicated and expensive. In a variation of this method, the reaction between the rare-earth metal and silicon is carried out in molten aluminium, and this method was tested by Brauer and Haag [1] for the preparation of cerium disilicide. An aluminium–cerium alloy containing ~10% Ce was fused with excess silicon in a corundum crucible at 900°, after which the alloy was treated first with acid and then with sodium hydroxide solution. The product obtained in this way, however, was found to be a ternary alloy of approximate composition $Ce_2Al_3Si_2$, so that $CeSi_2$ either is not formed or is formed together with the ternary alloy and is dissolved during the acid–alkali treatment of the fusion products. Thus attempts to prepare silicides by a method similar to Lebeau's copper–silicide method [23], used for the preparation of the silicides of *d*-transition metals, did not give satisfactory results.

Lanthanum disilicide has also been prepared by direct combination of the elements [3].

The reduction of oxides of the rare-earth metals with silicon is at present the most widespread method for preparing the silicides of many rare-earth metals. This method was proposed in its original form as early as 1902 by Sterba [23], who prepared cerium silicide by reducing CeO_2 with silicon:

$$CeO_2+3Si=CeSi_2+SiO_2 .$$

Further tests on this method [1,2] showed, however, that even after 10–40 min at 2000°–2400° in a tubular graphite resistance furnace the product is not $CeSi_2$ but a mixture of

cerium oxide, silicon carbide, and cerium silicate. The formation of the silicate was also observed by Walter[24] in a study of the reaction of CeO_2 with Si at 970°–1700°. Because of this, a vacuum method was developed[1]. This was designed to remove the volatile silicon monoxide, and, in the case of the preparation of cerium disilicide, is represented by the overall reaction:

$$CeO_2+4Si=CeSi_2+2SiO,$$

which according to Brauer and Haag passes through the following stages:

$$CeO_2+Si=Ce+SiO_2,$$
$$SiO_2+Si=2SiO,$$
$$Ce+2Si=CeSi_2.$$

This reaction scheme is not confirmed, however, by the later data of Neshpor and Samsonov[14], who prepared lanthanum silicide by this method. The manometric curve (Fig. 8) for the reaction

$$La_2O_3+7Si=2LaSi_2+3SiO,$$

shows not one pressure jump, as should be the case if Brauer and Haag's scheme (evolution of silicon monoxide) applies, but two. Moreover, the X-ray diffraction patterns of the specimens do not show lines corresponding to any of the modifications of SiO_2. An attempt to attribute the presence of the two pressure jumps to a stage in the reduction involving the formation of the lower lanthanum oxide LaO:

$$La_2O_3+Si \longrightarrow LaO+SiO,$$
$$LaO+Si \longrightarrow LaSi_2+SiO,$$

was also unsatisfactory, since the X-ray diffraction study of the reduction products obtained after the first pressure jump did not show the cubic lattice which should be exhibited by lanthanum monoxide LaO, by analogy with the lower oxides of other rare-earth metals, for example SmO and EuO,[7] and did not show the presence of metallic lanthanum in the reduction product. It was therefore suggested that the reduction takes place in two stages with the formation of lanthanum monosilicide as an intermediate product:

$$La_2O_3+5Si=2LaSi+3SiO,$$
$$2LaSi+2Si=2LaSi_2,$$
$$La_2O_3+7Si=2LaSi_2+3SiO.$$

This scheme is confirmed by the presence, in the X-ray diffraction patterns of the low-temperature products, of lines for both monosilicide and disilicide, and also by the results of a thermodynamic treatment of the manometric curve. On the basis of the above scheme, this treatment led to reasonable values for the heats of formation of LaSi and $LaSi_2$.

Brauer and Haag[1] prepared the disilicides of cerium (at 1550°), lanthanum, neodymium, praseodymium, samarium, ytterbium, yttrium, and scandium by reducing the oxides with excess silicon *in vacuo* and removal of the volatile silicon monoxide. The process was carried out in alumina tubes heated in tubular graphite resistance furnaces. The agreement between the compositions of the resulting disilicides and the calculated data is illustrated in Table 5.

Brewer and Krikorian[11] used an analogous method to prepare the silicides of many rare-earth metals, but these authors do not give the conditions and other characteristics of the processes used.

The silicides of lanthanum[14], cerium, and praseodymium have been prepared by the same method from a charge of stoichiometric composition, with heating for 30 min at 1550°–1600° and an initial pressure in the vacuum furnace of 10^{-3} mm Hg.

The vacuum-thermal method of preparing the disilicides of a number of rare-earth metals by reducing the oxides with silicon has also been used by Perri *et al.*[3] The purity of the oxides of lanthanum, cerium, praseodymium, samarium, europium, gadolinium, dysprosium, and yttrium was 99–99.5%, and that of the neodymium oxide was 95%. The reduction reactions were carried out in alumina boats *in vacuo* with continuous evacuation at 1100°–1600°. The optimum temperatures for the preparation were 1200°–1300° for $SmSi_2$ and 1400°–1550° for YSi_2 and $DySi_2$; increase in temperature above 1600° led to reaction with the material of the boat and contamination of the silicides.

Attempts by the same authors to prepare silicides by reducing the oxides with silicon in a medium of hydrogen did not give satisfactory results, due to the formation of films of silicon oxide on the silicide particles, giving products contaminated with considerable quantities of oxygen.

The electrolysis of melts. This method is analogous to the method for preparing borides, developed in detail by Andrieux. It was first used in 1865 by Ulik[25], who electrolysed fluoride melts. It was later applied to mixtures of CeO_2, SiO_2, and CaO by Sandlar[4]. This method has been studied in greatest detail by Dodero[26] for the case

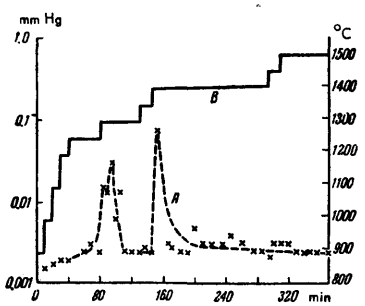


Fig. 8. Manometric curve for the reduction of lanthanum oxide with silicon in vacuo[14].

TABLE 5. Chemical analysis of specimens obtained by reducing oxides of the rare-earth metals with silicon.

Silicide	Metal, %		Silicon, %	
	calc.	expt.	calc.	expt.
$LaSi_2$	71.23	70.9	28.7	28.8
$CeSi_2$	71.43	72.1	28.57	27.6
$PrSi_2$	71.57	71.3	28.43	27.6
$NdSi_2$	71.99	70.7	28.01	27.8
$SmSi_2$	72.83	72.4	27.17	26.8
YSi_2	61.31	62.4	38.69	37.6

of the preparation of cerium and lanthanum silicides by the electrolysis of fused mixtures of oxides of the rare-earth metal, silicon, and calcium carbonate, chloride, and fluoride. A disadvantage of the method is that the silicides are usually contaminated with silicates, whose removal requires complex tedious operations, and this makes the electrolysis of melts unsuitable for the preparation of the silicides of the rare-earth metals.

4. SILICIDES OF SCANDIUM, YTTRIUM, AND THE LANTHANIDES

Scandium silicides. The first attempts to prepare scandium silicides by reducing scandium oxide with silicon *in vacuo* were made by Brauer and Haag[1], but the products could not be satisfactorily identified by X-ray diffraction methods. Preliminary analysis of the X-ray diffraction patterns showed that they differed considerably from those of the tetragonal disilicides of lanthanum and yttrium.

The experiments of Samsonov *et al.*[27] on the preparation of scandium mono- and di-silicides by reducing Sc_2O_3 with 98% silicon according to the reactions:

$$Sc_2O_3+5Si=2ScSi+3SiO,$$
$$Sc_2O_3+7Si=2ScSi_2+3SiO,$$

at 1100°–1900° showed that the X-ray diffraction patterns of the products of the reduction designed to produce $ScSi_2$ and those obtained at 1100°–1500° are identical, whereas those for the products at 1600°–1700° show some differences and are less distinct, apparently due to decomposition of the products with the liberation of silicon. The X-ray diffraction patterns of the products of the reduction designed to produce ScSi differ from the above patterns. Neither the first nor the second X-ray diffraction patterns could be identified. Chemical analysis of the products of the reduction designed to produce ScSi gives a composition close to this formula, but the products of the reduction designed to give $ScSi_2$ have a composition close to the formula Sc_3Si_5. A silicide of this composition is known for uranium, but the structure found for α-USi_2 has been attributed to it.

Yttrium silicides. The existence of three yttrium silicides, YSi, Y_5Si_3, and YSi_2, has been established. The latter is obtained by reducing yttrium oxide at 1400°–2250°[3] with silicon *in vacuo*[1,21]. The silicide YSi_2 crystallises in an orthorhombic lattice with the space group D_{4h}^{28} characteristic of the low-temperature α-modifications of the disilicides of the lanthanides (Table 1); β-YSi_2 has a tetragonal lattice of the α-$ThSi_2$ type (space group D_{4h}^{19}). The $\alpha \rightarrow \beta$ transformation takes place at 450°. The physical properties of YSi_2 have not been studied; it has been established, however, that it is paramagnetic down to 1°K.[19]

The monosilicide YSi was prepared[28] by arc melting and has a composition close to the stoichiometric. X-Ray diffraction study shows that YSi has an orthorhombic lattice belonging to the space group $Cmcm(D_{2h}^{1})$, similar to the CrB structure[29] and identical with the CaSi structure. The silicide Y_5Si_3 has a hexagonal lattice of the Mn_5Si_3 type[30].

Lanthanum silicides. The existence of two silicide phases — the monosilicide LaSi and the disilicide $LaSi_2$ — has been established in the lanthanum–silicon system.

Dodero[26] prepared lanthanum disilicide by the electrolysis of a mixture containing La_2O_3 10, SiO_2 30, $CaCO_3$ 50, CaF_2 78, and $CaCl_2$ 20 g at 1100° with a current of 30 A. After electrolysis for 1 h a pear-shaped deposit consisting of silicates with lanthanum silicide inclusions formed on the cathode. Since the chemical and mechanical separation of the resulting mixture is difficult, it is recommended that the electrolysis be carried out with a water-cooled aluminium cathode by the contact method; as electrolysis proceeds, the temperature is increased and the pear-shaped deposit drops into the melt, where the silicide collects in a fairly pure conglomerate. It is treated with 5% NaOH to remove free silicon.

Purer lanthanum silicide $LaSi_2$ is obtained by reducing lanthanum oxide with silicon *in vacuo*[1,3,21]. This process has been studied in greatest detail by Neshpor and Samsonov[14], who prepared lanthanum disilicide from a charge of stoichiometric composition, calculated on the assumption that the reaction

$$La_2O_3+7Si=2LaSi_2+3SiO$$

takes place.

To establish the optimum conditions for the reaction, the charge was formed into briquettes, placed in the graphite heater of a vacuum resistance furnace, and heated at temperatures in the range 1200°–1600° for 30 min at each temperature. The initial pressure in the furnace was 10^{-3} mm Hg. The extent to which the reaction had proceeded was found by chemical analysis and X-ray diffraction, and also from the value of the ratio $\gamma = (G_1/G_2) \times 100\%$, where G_1 is the weight of product which would be obtained if the reaction went to completion according to the equation and G_2 the actual weight of reaction product obtained at each temperature. Values of $\gamma \leq 100\%$ correspond to more or less complete reaction. The results of the chemical analysis and X-ray diffraction study of the products obtained at different temperatures are given in Table 6 and Fig. 9.

The data in Table 6 show that the reaction with silicon begins at temperatures below 1250°. The quantity of free silicon decreases fairly rapidly with increase in temperature, but even at 1580° the reaction product still contains oxygen, whose concentration can be estimated approximately from the difference 100 - (La + Si_{total}). The X-ray diffraction data show that $LaSi_2$ has appeared in the reaction products at 1250°, and the concentration of this phase increases with temperature. In addition to $LaSi_2$, however, the X-ray diffraction patterns show the presence of

TABLE 6. Chemical and phase composition of the products of the reduction of lanthanum oxide by silicon (duration of reaction 30 min).

Temperature, °C	γ, %	Chemical composition, %					Phase composition
		La	Si_{total}	Si_{free}	$Si_{combined}$	100−(La+Si_{total})	
—	—	71.3*	28.7*	—	28.7*	—	$LaSi_2$
1250	104	53.0	37.25	22.3	19.25	9.75	$LaSi_2$, Si, phase X
1260	101	51.0	36.80	22.1	18.87	11.61	
1370	87	50.5	30.6	13.65	19.65	9.9	
1400	75	61.4	28.75	1.6	27.6	9.85	
1490	72	67.3	27.2	1.3	26.3	5.5	$LaSi_2$, phase X
1580	78.7	65.0	28.8	—	—	6.2	

* Calculated composition of $LaSi_2$.

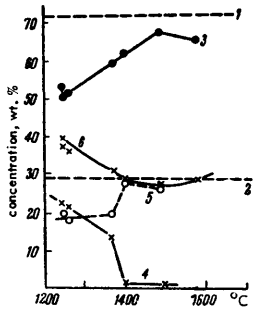


Fig. 9. Temperature dependence of the composition of the products of the reduction of lanthanum oxide with silicon: 1) and 2) concentration of La and Si, respectively, in $LaSi_2$. Experimentally determined concentrations of La and Si in the reaction products: 3) La; 4) Si_{free}; 5) $Si_{combined}$; 6) Si_{total} (duration of reaction 30 min [14]).

a phase X, whose concentration is a maximum in the low--temperature products and decreases with increase in the reaction temperature.

Change in the duration of the reaction leads to the results shown in Fig. 10. Heating was continued until the pressure in the furnace was approximately equal to that at the start of the reaction. A sharp increase in pressure, corresponding to the vigorous evolution of SiO, is observed from 1400°. Table 7 gives the results of the chemical analysis and X-ray diffraction study of the reaction products and also shows the time required for the pressure in the furnace to reach a value close to the initial value. Fig. 11 gives the temperature dependence of the composition and the time required for the reaction to proceed to an appreciable extent.

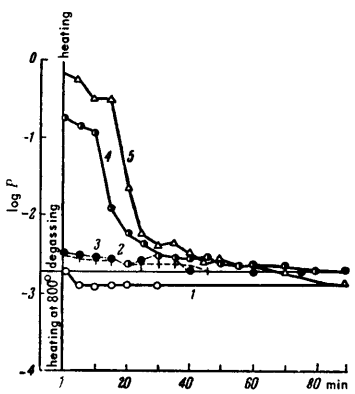


Fig. 10. Isotherms for the pressure in the furnace during the reduction of lanthanum oxide by silicon [14]: 1) 1150°; 2) 1250°; 3) 1375°; 4) 1490°; 5) 1600°.

TABLE 7. Dependence of the chemical and phase composition of the products of the reduction of lanthanum silicide with silicon on the temperature and duration of heating *in vacuo*.

Temperature, °C	Time, min	γ, %	Chemical composition, %					Phase composition
			La	Si_{total}	Si_{free}	$Si_{combined}$	100 − (La + Si_{total})	
1150	30	120	50.0	40.25	26.0	19.25	9.75	$LaSi_2$, Si, phase X
1250	45	118	50.7	40.3	24.4	21.08	9.00	
1375	70	75	66.5	28.9	3.6	26.3	4.6	
1490	90	81	63.75	31.0	2.7	29.1	5.25	$LaSi_2$, phase X
1600	100	53.5	70.20	28.4	0	28.4	1.4	$LaSi_2$

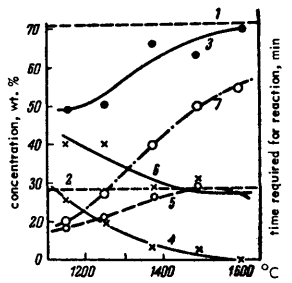


Fig. 11. Temperature dependence of the composition of the products of the reduction of lanthanum oxide with silicon and the temperature dependence of the time required for the reaction [9]. Symbols as in Fig. 9; 7) time, h.

These results show that the optimum conditions for the preparation of lanthanum disilicide are obtained at 1600° for 1.5 h. Under these conditions, pure lanthanum oxide gives a silicide of composition: La 70.9, $Si_{combined}$ 28.1, and C (from the graphite heater) 0.15%.

A manometric study of the reduction process indicated that phase X, formed at relatively low temperatures, is lanthanum monosilicide.

Pure lanthanum disilicide $LaSi_2$ can also be obtained by the direct reaction between lanthanum and silicon [3].

Lanthanum disilicide is known in only one crystalline modification — a tetragonal form for which the following lattice constants have been given:

a, Å	c, Å	c/a	References
4.280	13.747	3.21	1
4.374	13.565	3.12	31
4.31	13.80	3.21	3

The most reliable data are those of Perri *et al.*[3], and these are generally accepted.

The data obtained by Neshpor and Samsonov [14] and Binder [21] for the resistivity of $LaSi_2$ differ considerably, the values being 536 and 273 μΩ cm respectively. The electrical conductivity of $LaSi_2$ changes character at 500°.

Below 500° $LaSi_2$ is an *n*-type metallic conductor and above 500° a *p*-type semiconductor. Like scandium and yttrium disilicides, $LaSi_2$ is paramagnetic down to 1°K. It is oxidised extensively in air at 1300°. Lanthanum silicide differs from the other silicides of the rare-earth metals in its relatively low hardness (31 R_A [21]‡) and a bending strength§ of $\sigma_{bending}$ = 27.2 kg mm^{-2}.

Cerium silicides. The equilibrium diagram of the cerium–silicon system was first studied by Vogel[22], who detected one silicide phase — the monosilicide CeSi — and constructed a tentative diagram. The existence of a second silicide phase $CeSi_2$ was then discovered[1,23,32], and later Brewer and Krikorian[11] made a fairly detailed study of the system. X-Ray diffraction study of the alloys, which they prepared by sintering metallic cerium with silicon powder, showed the presence of phases with nominal formulae $CeSi_{0.35}$ (Ce_3Si), $CeSi_{0.5}$ (Ce_2Si), and $CeSi_{0.75}$. The phase $CeSi_{0.35}$ is detected in the alloys containing unreduced CeO_2, the phase $CeSi_{0.5}$ in alloys containing 33–37 at.% Si, and the phase $CeSi_{0.75}$ in alloys with 40–45 at.% Si.

Brewer and Krikorian also confirmed the presence, in addition to these phases, of the disilicide $CeSi_2$ with tetragonal lattice and constants a = 4.175 ± 0.002 Å and c = = 13.878 ± 0.006 Å (the specimens of $CeSi_2$ were contaminated with up to 5% C), which differ slightly from the results of Brauer and Haag[1] and Zachariasen[32] and more significantly from those of Perri *et al.*[3] and Binder[21]. The latter are now generally accepted:

a, Å	c, Å	c/a	References
4.175	13.848	3.32	11
4.16	13.90	3.34	32
4.156	13.84	3.33	1
4.27	13.88	3.26	3.21

According to Parthé[28], cerium monosilicide, CeSi, has an orthorhombic lattice of the FeB type. No phase transformations have been observed in $CeSi_2$.[5] Part of the cerium–silicon diagram, constructed from results from various sources[11,22,33], is shown in Fig. 12.

$CeSi_2$ can be prepared directly from the elements at 1430°[22] or by electrolysis of fused mixtures of CeO_2, SiO_2, and CaO [4] or of CeO_2, SiO_2, CaF_2, and $CaCl_2$,[26] but is usually prepared by reducing cerium oxide with silicon *in vacuo* at 1550°–1600° with subsequent extraction of silicon if excess of the latter is used in the reduction[1,3,21].

Thus Brauer and Haag[1] prepared cerium disilicide from CeO_2 + Si mixture with excess silicon (1 : 7) by heating in an alundum tube placed in a tubular graphite furnace at 1550°, with evacuation of the silicon monoxide with a vacuum pump. The reaction was assumed to be complete when a fairly sharp drop in pressure was observed. The reaction products were treated with 2 *N* sodium hydroxide solution until evolution of hydrogen stopped.

Cerium disilicide is slightly harder than lanthanum disilicide. Its electrical resistivity at room temperature is ~400 μΩ cm, and preliminary results[14] indicate that in the range 20°–1000° $CeSi_2$ has a negative temperature coefficient of resistivity, *i.e.* it exhibits semiconducting properties. It is paramagnetic down to ~1°K.[19]

‡ R_A means Rockwell A superficial hardness.

§ Transverse rupture strength at room temperature (Ed. of Translation).

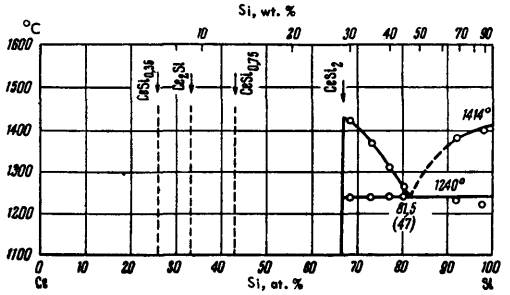


Fig.12. Equilibrium diagram of the cerium–silicon system[33].

Brewer and Krikorian[11] made a preliminary study of the phase compositions of some alloys in the Ce–Si–C system. An X-ray diffraction investigation of an alloy containing C 25, Ce 25, Si 50%, obtained from the elements by sintering at 1330° for 44 min, revealed the phase $CeSi_2$ and another phase, whose composition and structure was not determined[7]. Cerium carbides CeC, Ce_2C_3, and CeC_2 were not detected. The alloys obtained were greyish brown. The Ce–Si–C alloys decomposed in air with the liberation of acetylene.

Praseodymium silicides. Praseodymium has been shown to form one silicide phase — the disilicide $PrSi_2$ — which has an orthorhombic lattice of the YSi_2 type (α-$PrSi_2$) up to -120° and the tetragonal lattice of the $ThSi_2$ type (β-$PrSi_2$), characteristic of the disilicides of the rare-earth metals, above -120°. The transformation is accompanied by extremely small changes in the constants a and c.

$PrSi_2$ has the lowest resistivity in the $LaSi_2$–$CeSi_2$–$PrSi_2$ series, the value being ~200 μΩ cm, and is as yet the only disilicide for which ferromagnetism has been detected at very low temperatures[19]; its Curie point is 10.5°K.

Praseodymium disilicide is prepared by reducing praseodymium oxide with silicon *in vacuo* at 1550°–1600°.[1,3]

Neodymium silicides. Perri *et al.*[3] report an orthorhombic structure for neodymium silicide, and Brauer and Haag[1] a tetragonal structure. Although there are no published data on phase transformations in $NdSi_2$, it may be assumed that the compound exists in the α- and β-modifications characteristic of the neighbouring disilicides of praseodymium and samarium. $NdSi_2$ is obtained by reducing neodymium oxide with silicon *in vacuo*[1,3,21]. According to Binder[21], the resistivity of $NdSi_2$ is ~350 μΩ cm and the bending strength has the low value of 6.2 kg mm^{-2} at 20°. Neodymium disilicide is paramagnetic down to 1°K.[19]

Samarium silicides. Samarium disilicide is known in two crystalline modifications: α-$SmSi_2$ and β-$SmSi_2$, with lattices of the YSi_2 orthorhombic and $ThSi_2$ tetragonal types respectively and a transformation temperature of 380°. $SmSi_2$ is prepared by reducing samarium oxide with silicon *in vacuo* at 1550°–1600°.[1,3] According to Perri *et al.*[3], the optimum temperature of formation of $SmSi_2$ by this method lies in the range 1200°–1300°.

Europium silicides. Europium forms the disilicide $EuSi_2$, which exists in the tetragonal modification. No orthorhombic modification of $EuSi_2$ has been detected[5], even below -150°. Europium disilicide is prepared by reducing europium oxide with silicon *in vacuo*[1,21].

The lattice constants of $EuSi_2$ are anomalous, being much higher than those of the disilicides of the neighbouring elements samarium and gadolinium. This is apparently due to the bivalency of europium in the disilicide and is discussed in detail above (p.703). $EuSi_2$ melts at a lower temperature (1500°) than the disilicides of the other lanthanides.

Gadolinium silicides. Gadolinium forms one silicide, known in two crystalline modifications: the orthorhombic α-$GdSi_2$ and the tetragonal β-$GdSi_2$, with transformation temperature[5] 400°.

The calculations of Perri *et al.*[3] of the structure factor of gadolinium silicide showed that agreement between the calculated and experimental values is obtained only by assuming for the silicide phase the composition $GdSi_{1.3}$. The pyknometric density of this silicide is 5.94 g cm^{-3}, whereas the density calculated for $GdSi_2$ is 6.43 g cm^{-3} and that for $GdSi_{1.4}$ 5.92 g cm^{-3}. Chemical analysis showed an Si : Gd atomic ratio of 1.47. On this basis it was suggested that a gadolinium silicide phase $GdSi_{1.4}$, with a certain homogeneity range, exists.

Gadolinium silicides are prepared by reducing gadolinium oxide with silicon *in vacuo* at 1550°–1600°.[3,21] The reduction of gadolinium oxide with silicon[27]:

$$Gd_2O_3+Si \longrightarrow GdSi_2+SiO\,,$$

takes place in 40 min at 1500° in a vacuum resistance furnace with graphite heater, to give a product containing 26.8% Si (calculated for $GdSi_2$: Si 26.3%) and 0.8–0.9% C. X-Ray diffraction study showed that the lattice corresponds to the structure of orthorhombic $GdSi_2$.

Binder[21] noted that $GdSi_2$ exhibits a range of homogeneity, whose width was not defined precisely. The resistivity of $GdSi_2$ is ~260 $\mu\Omega$ cm. Its bending strength is the lowest of any disilicide yet studied and amounts to only 4.4 kg mm^{-2}.

There are no data on silicides of terbium, holmium, erbium, thulium, and lutetium.

Dysprosium silicides. Dysprosium disilicide exists in two crystalline modifications: the orthorhombic α-$DySi_2$ and the tetragonal β-$DySi_2$, with the $\alpha \rightarrow \beta$ transformation at 540°.[5] Like the disilicides of the other lanthanides, $DySi_2$ is prepared by reducing the oxide with silicon *in vacuo*[21]. According to Perri *et al.*[3], the optimum temperature for the reduction is 1400°–1500°. The properties of this disilicide have been studied in more detail than those of the disilicides of the other later lanthanides (Tb... Lu), since it has possible uses in nuclear technology, in counters and tracers.

The density of the orthorhombic modification of $DySi_2$, determined by X-ray studies, is 6.80 g cm^{-3}, with the assumption that it has the orthorhombic lattice characteristic of the disilicides, with four atoms in the unit cell. This value differs considerably, however, from the pyknometric value of 5.10 g cm^{-3}, and this has been attributed to the existence of a large number of vacant sites. This is also indicated by the high resistivity of $DySi_2$, the value being 3020 $\mu\Omega$ cm, which is greater by one order of magnitude than that of other lanthanide disilicides. $DySi_2$ has a positive temperature coefficient of resistivity, of the same order of magnitude as that of metals. According to Binder and Steinitz[16], dysprosium disilicide is extremely hard (89 R_A), and its bending strength at room temperature is 6.68 kg mm^{-2}.

$DySi_2$ is stable in boiling water, treatment for 16 h leading to no measurable change in weight of the specimens. $DySi_2$ is extremely stable to oxidation at 1000° (Fig.6):

Duration of oxidation, h	Change in weight, mg cm^{-2}
0.5	+2.60
1	+4.34
18	+21.4
42	+35.8
66	+44.5
96	+52.2
398	+80.0
782	+90.8

Even after prolonged oxidation at 1000°, the disilicide specimen remains hard and compact, and retains its silvery colour.

Articles made of $DySi_2$ can be produced either by hot pressing or by making use of its relatively low melting point of 1550° and sintering the previously compressed objects. The sintered articles can be shaped with silicon carbide wheels and cut with abrasive wheels or by electro-impulse methods. The usual precautions necessary when working with hard and brittle materials must be taken.

Ytterbium silicide. An attempt has been made to prepare ytterbium disilicide by reducing ytterbium oxide with silicon at 1550°–1600°.[1] However, X-ray diffraction study of the specimen was impossible; preliminary results showed that the ytterbium silicide was of indefinite composition, $YbSi_x$ obtained in this work crystallised in a lattice different from that of the other tetragonal lanthanide disilicides. In our opinion, the X-ray diffraction pattern shows a similarity to those of the orthorhombic modifications of the disilicides.

5. USES

The fields of applications of the silicides of the rare-earth metals have not yet been fully determined, but examination of their physicochemical properties reveals the following possible uses.

The comparatively high heat resistance of some silicides, combined with the high neutron-capture cross-section of elements such as Gd and Eu indicates their possible use, either directly or as additives in other alloys, as materials for various neutron-absorbing devices in nuclear-energy technology[16]. The half-lives of the silicides of some metals in the radioactive state, for example, dysprosium, are convenient for practical purposes, and this makes it possible to use them for the construction of dosimeters and counters[21]. The semiconducting properties of some of the silicides (those of lanthanum and cerium), combined with their chemical stability, makes it possible to use these silicides as semiconducting materials for use at high temperatures or in aggressive media. The comparatively low

thermodynamic stability of the silicides and the high affinity of the components for oxygen reveals a possible application for deoxidising in metallurgy and as special hardeners for introducing the rare-earth metals into various types of glass. Individual silicides are probably of interest as scale-resistant components in alloys with high-temperature strength.

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THE MOLECULAR STRUCTURE OF 1,3,5-TRIAZINE AND ITS DERIVATIVES

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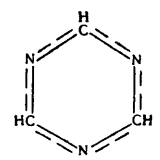
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1. INTRODUCTION

One of the sensational scientific achievements of recent years has been the long awaited discovery of free symmetrical triazine. It has turned out that this compound was first obtained by Nef[1] as early as 1895, but owing to errors in determining its molecular weight, he ascribed to this substance an incorrect structural formula, regarding it as a dimer of hydrocyanic acid. This view was shared by other investigators for more than half a century (see, for example, Hinkel and Summers[2]).

It was only in 1953 that Grundmann and Kreutzberger[3] again determined the molecular weight of the product described by Nef, and found, to their surprise, that it was a trimer of hydrocyanic acid, its molecular structure being that of symmetrical triazine (I):



(I)

Intensive research on the physicochemical properties of 1,3,5-triazine gave an immense amount of information, not yet fully systematised, which enables a fairly complete picture to be obtained of its molecular structure, which is of considerable theoretical importance.

Many derivatives of 1,3,5-triazine are of no less theoretical and practical interest. Thus melamine (2,4,6-triamino-1,3,5-triazine), cyanuric acid (2,4,6-trihydroxy--1,3,5-triazine), cyanuric chloride (2,4,6-trichloro-1,3,5--triazine), and several others have become of definite and