actions similar to that employed for the preparation of the mono derivative

$$3CH_3NH_2\cdot HCl + 3BCl_3 \longrightarrow (CH_3NBCl)_3 + 9HCl^{16}$$

$$BrCF{=}CF_2 + Li(CH_2)_3CH_3 \longrightarrow LiCF{=}CF_2 + Br(CH_2)_3CH_3^{15}$$

$$(CH_3NBCl)_3 + 3LiCF{=}CF_2 \longrightarrow (CH_3NBCF{=}CF_2)_3 + 3LiCl$$

The apparatus and procedure for the preparation of this compound were identical with the procedure used for the preparation of B,B′-dimethyl-B″-perfluorovinyl-N,N′,N″ trimethylborazine. Three grams of B-trichloro-N-trimethylborazine, 0.87 g of methyllithium, and 7.0 g of perfluorovinyl bromide yielded 2 ml of pale yellow liquid. This liquid was then purified by vpc.

The purified product was identified by infrared spectrophotometry, mass spectrometric analysis, nuclear magnetic resonance, and element analysis as B,B′,B″ tris(perfluorovinyl)-N,N′,N″-trimethylborazine.

The observed vibrational frequencies of B,B′,B″-tris(perfluorovinyl)-N,N′,N″-trimethylborazine are: 2941 (m), C–H str; 1740 (s), C=C str; 1479 (vs), asym CH_3 def; 1450 (vs), B–N str; 1400 (vs), sym CH_3 def; 1316 (sh), 1282 (vs), 1176 (m), 1099 (ms), 1042 (s), 950 (s), N–CH_3 def; 735 (ms), B–N def; 725 (ms), B–N def.

The mass spectrometric analysis showed a molecular ion at m/e 363. The isotope ratios indicated that the compound contains three boron atoms and no chlorine. The mass fragmentation pattern was consistent with the postulated structure.

The element analysis is also consistent with the calculated values. *Anal.* Calcd: B, 8.94; N, 11.59; C, 29.81; F, 47.15; H, 2.51. Found: B, 8.2; N, 11.15; C, 29.32; F, 47.30; H, 2.89.

The ^1H nmr spectrum contained only one broad peak at 3.28 ppm. This is compatible with methyl bonded to a nitrogen atom. Methyl bonded to a boron atom should give resonance at higher field.

The ^{19}F spectrum contained three peaks of equal intensity: A, +95.7 ppm; B, +117.2 ppm; C, +195.3 ppm. The coupling constants for J_{ab}, J_{ac}, and J_{bc} were found to be 72.7, 23.7, and 115.8 Hz, respectively. These data support the presence of the perfluorovinyl group[17] and further indicate that all such groups are equivalent.

The ^{11}B spectrum contained one very broad peak (about 1000 Hz wide) around −18 ppm. This broadness could arise either from a large quadrupole coupling constant or from boron–nitrogen coupling.

All spectra were determined with a Varian HR-60 spectrometer. The ^1H spectrum was recorded at 60 MHz and referenced to tetramethylsilane, the ^{19}F at 56.4 MHz and referenced to $CFCl_3$, and the ^{11}B at 19.3 MHz and referenced to external boron trifluoride etherate.

B,B′,B″-Tris(perfluorovinyl)-N,N′,N″-trimethylborazine hydrolyzes readily in moist air but is thermally stable to temperatures exceeding 300°. The product melts at −50° and the extrapolated boiling point is 526°. The temperatures and vapor pressures are: 28.2°, 5.00 mm; 40.2°, 6.90 mm; 51.5°, 10.10 mm; 61.2°, 14.85 mm; and 71.1°, 22.00 mm.

The vapor pressure between 71.1 and 28.2° can be expressed by

$$\log P_{\mathrm{mm}} = 5.865 - \frac{1571}{T(^{\circ}\mathrm{K})}$$

This work demonstrates that perfluoro groups can be bonded to the boron atoms of a borazine ring and the resulting configurations are thermally stable to temperatures exceeding 300°.

In contrast to the mono-, bis-, and trisperfluorovinylboranes described by Stafford and Stone[10] which decompose readily to liberate boron trifluoride, the perfluorovinylborazines are considerably more stable thermally, undoubtedly owing to the contributions of the B–N ring. When a sample of B,B′-dimethyl-B″-perfluorovinyl-N,N′,N″-trimethylborazine purified by vapor phase chromatography was heated to 482° for 2 hr, the gaseous decomposition products consisted of methane and hydrogen; there was no evidence of boron trifluoride.

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(16) G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *J. Am. Chem. Soc.*, **80**, 4515 (1958).

(17) J. W. Emsley, J. Feeney, and L. K. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Ltd., London, 1966, p 907.

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Dimorphism of Rare Earth Disilicides

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The preparation and crystal structures of the rare earth disilicides has been the subject of a number of works.[1–4] The preparation of these compounds was carried out by direct reaction of the two metals in the proper atomic ratio, or by silicon reduction of the metal oxides.

In relation to their crystal structures, rare earth disilicides can be classified into three structure types: $ThSi_2$-type tetragonal form (La–Pr, Eu), a slightly distorted orthorhombic version of the $ThSi_2$ structure (Nd–Ho, α-Y), and AlB_2-type hexagonal form (Er–Lu, β-Y).

Studies of the stoichiometric composition of the rare earth disilicides have shown deficiency of silicon in the La–Ho series ($GeSi_{1.4}$). In the case of the hexagonal disilicides, the metal : silicon ratio for the ytterbium compound has been found to be 1 : 2.

The polymorphism of the La–Dy disilicide was studied by Perri, *et al.*[5] High-temperature X-ray study of these compounds has shown transformation of the orthorhombic disilicides to tetragonal form in the temperature range 400–600°. In those cases when the tetragonal form is the stable one at room temperature, the orthorhombic version was obtained below room temperature (−120 to 150°).

Dimorphism was observed in the case of YSi_2.[3] This compound, when prepared at 1100°, crystallizes in the AlB_2-type structure and by heating to 1500° changes to the orthorhombic form. Similar dimorphism has been observed for $ThSi_2$[6] and USi_2.[7]

A new method of preparation of the rare earth disilicides was devised by the present authors.[8] In this

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(1) G. Brauer and H. Haag, *Z. Anorg. Allgem. Chem.*, **267**, 198 (1952).

(2) J. A. Perri, I. Binder, and B. Post, *J. Phys. Chem.*, **63**, 616 (1959).

(3) I. P. Mayer, E. Banks, and B. Post, *ibid.*, **66**, 693 (1962).

(4) A. G. Tharp, *ibid.*, **66**, 758 (1962).

(5) J. A. Perri, E. Banks, and B. Post, *ibid.*, **63**, 2073 (1959).

(6) A. Brown, *Acta Cryst.*, **14**, 860 (1961).

(7) W. H. Zachariasen, *ibid.*, **2**, 94 (1949).

(8) I. Mayer, E. Yanir, I. Shidlovsky, and A. Glasner, The International Congress of the International Union of Crystallography, Moscow, 1966, in press.

method, the disilicides are prepared at relatively low temperatures (maximum 500°) from their amalgams. This method enables us to study the properties of the rare earth disilicides at much lower temperatures than in previous investigations. Consequently, the dependence of crystal structure on temperature and atomic size, the study of which is the aim of this work, could be more thoroughly investigated.

Experimental Section

Preparation.—The rare earth disilicides studied in this work were prepared by an amalgamation process.

Mixtures of the rare earth metals (99.9% pure), silicon, and mercury were heated in an evacuated Vycor tube in an electric furnace at approximately 450°, for 10–12 hr. Mercury was then separated from the above mixture by distillation in a bent tube. After all the mercury had collected in the cooler part of the tube, annealing of the samples in the hot part of the tube was carried out at 450–600° for 10–12 hr. Well-crystallized samples were obtained by this method. Attempts to prepare the samarium compound were unsuccessful. The X-ray patterns of the samples were completely free from lines of any rare earth mercury compound, but lines of metallic oxides and silicon sometimes appeared.

The disilicides prepared by the amalgamate method were studied at elevated temperatures. This was achieved by induction heating in tantalum boats under a protective atmosphere of argon or helium, the maximum temperature being 1600°.

X-Ray analyses of the samples were carried out by the powder diffraction method, using a Phillips diffractometer with filtered Cu Kα radiation.

Results

Crystal data of rare earth disilicides prepared by the amalgamate process are listed in Table I. The maximum deviation in the lattice parameters was ±0.003 A. Numbers in parentheses in Table I are the lattice constants found for these compounds when prepared at 1600°. These results show that the disilicides of La–Nd (except Ce) have the GdSi$_2$-type orthorhombic structure, while the corresponding Gd–Lu and Y compounds crystallize in the AlB$_2$-type hexagonal form.

Table I

Crystal Data for Disilicides

Disilicide of	Crystal system	Lattice constants a	b	c
La	Orthorhombic	4.27	4.19	13.94
Ce	Tetragonal	4.19	...	13.94
Pr	Orthorhombic	4.17	4.12	13.82
Nd	Orthorhombic	4.17	4.13	13.65
Gd	Hexagonal	3.87		4.17
Tb	Hexagonal	3.84		4.14
Dy	Hexagonal	3.83		4.12
Ho	Hexagonal	3.80		4.10
Er	Hexagonal	3.78 (3.78)		4.08 (4.09)
Tm	Hexagonal	3.77 (3.76)		4.07 (4.07)
Lu	Hexagonal	3.75 (3.74)		4.05 (4.04)
Y	Hexagonal	3.83 (3.85)		4.14 (4.14)

Table II

Structure Changes of Rare Earth Disilicides at 1600°

Disilicide of	Structure: Amalgamate method	After heating up to 1600°
La	Orthorhombic	Tetragonal
Ce	Tetragonal	Tetragonal
Pr	Orthorhombic	Tetragonal
Nd	Orthorhombic	Orthorhombic
Gd	Hexagonal	Orthorhombic
Tb	Hexagonal	Orthorhombic
Dy	Hexagonal	Orthorhombic
Ho	Hexagonal	Orthorhombic
Er	Hexagonal	Hexagonal
Tm	Hexagonal	Hexagonal
Lu	Hexagonal	Hexagonal
Y	Hexagonal	Orthorhombic

Table II contains the results obtained by heating the above disilicides to 1600°. As a result of heating, two kinds of changes occurred: (1) orthorhombic (distorted ThSi$_2$ type) → tetragonal (ThSi$_2$ type) (heated to 1600°) in the case of LaSi$_2$ and PrSi$_2$; (2) hexagonal (AlB$_2$ type) → orthorhombic (distorted ThSi$_2$ type) (heated to 1600°) in the cases of Gd–Ho and Y disilicides.

The composition of the compounds was proved by their X-ray pattern. In case of the La–Nd disilicides, lines of elementary silicon appeared on the X-ray pattern while lines of metals or metallic oxides were absent. These observations, together with the facts that the maximum temperature (600°) used in the present method of preparation excludes the possibility of formation of silicides by reaction between the starting materials and the reaction vessel and also that rare earth metals do not evaporate at this temperature, led us to the conclusion that the La–Nd compounds are not true disilicides.

In the case of the Gd–Lu and Y disilicides, silicon lines were absent; thus these compounds crystallize in the stoichiometric composition of MSi$_2$.

Discussion

Results obtained in the present study prove the dimorphism already known for La–Pr disilicides and extend the dimorphism of the hexagonal disilicides known for YSi$_2$ to the Gd–Ho disilicides.

The main difference between the ThSi$_2$ and AlB$_2$ structures is in the arrangement of the silicon atoms within the silicide compound. In the AlB$_2$-type structure silicon atoms are arranged in a layer structure similar to graphite, whereas in the ThSi$_2$-type tetragonal and orthorhombic structure a three-dimensional silicon network is present.

The dimorphism orthorhombic → tetragonal (heated to 1600°) found in this work shows close similarity to that obtained by Perri, *et al.*,[5] in different conditions. In both cases the orthorhombic form appears to be the low-temperature form. In a recent work[9] the orthorhombic version was obtained for "CeSi$_2$" by lowering the silicon content of the compound to CeSi$_{1.3}$ which progressively changes to the tetragonal form at the composition CeSi$_{1.7-2.0}$. These results indicate that lowering the temperature of preparation or the silicon content of the compound affects structure in the same manner as a decrease in the atomic size of the metal. In both cases the orthorhombic structure is favored.

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(9) B. Aronsson, T. Lundstrom, and S. Rundquist, "Borides, Silicides and Phosphides," Methuen and Co. Ltd., London, 1965, p 21.

The AlB_2 hexagonal disilicides can be divided into two groups. The Gd–Ho and yttrium compounds are stable only at relatively low temperatures, while in the case of Er–Lu compounds, the hexagonal structure is the stable one up to 1600°.

Atomic size and composition appear to be the main factors in the formation of the AlB_2-type structure found for the lanthanide disilicides. In Table III interatomic distances found for the hexagonal disilicides are given. Table III shows that only when the ratio r_{Si}/r_M is more than 0.579 can the AlB_2-type structure be formed (Dy being an exception) while the $ThSi_2$ phase is formed at lower ratios. Since in this structure metal atoms form intermediate layers between the silicon sheets, metal atoms with too large size cannot be placed between the silicon sheets, and their disilicides do not crystallize in the hexagonal structure. The Gd–Ho and yttrium compounds appear to form an intermediate group according to their size where the structure equilibrates between a low-temperature hexagonal and high-temperature orthorhombic form. It is noteworthy that in the hexagonal–orthorhombic dimorphism, the orthorhombic version is always the stable one at high temperatures, having also the higher melting point as was found for the orthorhombic version of USi_2. Er–Lu disilicides having the smallest metal atoms among the lanthanides crystallize in the hexagonal structure at low as well as at high temperatures.

TABLE III

	Interatomic dist, A		Atomic radii, A		
	M–Si	M–M	r_M	r_{Si}	r_{Si}/r_M
Gd	3.054	3.867	1.934	1.120	0.579
Tb	3.036	3.843	1.922	1.114	0.580
Dy	3.022	3.829	1.915	1.107	0.578
Ho	3.003	3.800	1.900	1.103	0.581
Er	2.990	3.783	1.892	1.098	0.580
Tm	2.980	3.770	1.885	1.095	0.581
Lu	2.963	3.748	1.874	1.089	0.581
Y	3.030	3.834	1.917	1.113	0.581

The Gd–Ho disilicides crystallize in the hexagonal form also when heated to high temperature,[10] provided there is an average composition of M_3Si_5, thus indicating that when vacancies are present in the silicon layer, the AlB_2-type structure can be obtained at these conditions (high temperature).

[10] C. A. Lundin, "Rare Earth Research," The Macmillan Co., New York, N. Y., 1961, p 306.

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Halogenation of Silanes by Silver Chloride and Silver Bromide

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Halosilanes can be prepared by the reaction between silane and the appropriate hydrogen halide over an aluminum halide catalyst at 100°.[2] Chlorodisilane has been prepared in about a 3% yield from disilane at room temperature in 8 hr while bromodisilane was obtained in an 18% yield in only 5 min at −78°.[3] A large excess of silane or disilane is required to minimize the formation of the polyhalo derivatives.

Recently, chlorogermane and bromogermane have been obtained in 71 and 30% yields by the reaction between germane and silver chloride or bromide at 250–260°. Similarly, chlorodigermane and bromodigermane were prepared in 26 and 40% yields by reactions with digermane at 90°. In all of these reactions, the germanes were pumped over the appropriate silver salt in a heated tube.[4]

The liquid–solid phase reaction between diethylsilane and silver chloride to produce diethylchlorosilane has also been observed.[5]

In this Note we report our results on the gas–solid phase reactions between silanes and silver chloride or bromide.

Experimental Section

These reactions were carried out with standard high vacuum techniques. Separations were made by trap to trap distillations through traps cooled by standard slush baths. Silane, disilane, and the methylsilanes were prepared by reduction of the corresponding chloro compounds with lithium aluminum hydride.[6] The starting materials were treated with wet 1,2-dimethoxyethane to remove the last traces of HCl.

The reaction vessel consisted of a 100-ml bulb sealed to a Pyrex tube (18 mm o.d.) with a constriction 13 cm above the bulb. A glass wool plug at the constriction retained the silver salt which was held in five layers by glass wool plugs. The salt was heated by a heating tape wrapped around the reaction tube. A standard taper joint, 21 cm above the constriction, connected the reaction system to the vacuum line through a stopcock located above the joint. The temperatures were measured by a standard thermometer in a glass well located between the heating tape and the outer insulation.

The products and reactants were identified and checked for purity by infrared and vapor pressure measurements. The hydrogen chloride fractions (passing a trap cooled to −130° and condensed in a trap cooled to −160°) were considered pure when no Si–H stretching frequency ($\sim$2180 cm^{-1}) was observed. The final separation of hydrogen chloride from silane or disilane was carried out in wet 1,2-dimethoxyethane. The small fractions retained in this solvent were assumed to be hydrogen chloride.

Proton nmr spectra were obtained on neat samples with $Si(CH_3)_4$ at 0.00 as an external standard. Absorptions with a minus (−) sign were downfield.

(1) **SiH_4–AgCl Reaction.**—Silane (1.02 mmoles) was distilled through 22.5 g of silver chloride, heated to 260°, and condensed in the bulb with liquid nitrogen. The volatile fraction was then redistilled through the heated salt and condensed into a trap in the vacuum system with liquid nitrogen. The volatile fraction now consisted of silane (0.59 mmole), 0.38 mmole of chlorosilane (vapor pressure 55 torr at −78°, lit.[2] 56 torr), dichlorosilane (0.075 mmole), and hydrogen chloride (0.54 mmole).

(2) **Si_2H_6–AgCl Reaction.**—Disilane (2.46 mmoles) was passed through the reaction tube (at room temperature) and condensed

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[1] To whom inquiries concerning this Note should be sent.

[2] A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

[3] M. A. Abedini, C. H. Van Dyke, and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **25**, 307 (1963).

[4] K. M. MacKay, P. Robinson, E. J. Spanier, and A. G. MacDiarmid, *ibid.*, **28**, 1377 (1966).

[5] H. H. Anderson, *J. Am. Chem. Soc.*, **80**, 5083 (1958).

[6] A. E. Finholt, A. C. Bond, K. E. Wizbach, and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947).