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Preparation, Identification and Chemical Properties of the Niobium Germanides[1,2]

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An X-ray diffraction investigation establishes the existence of compounds of compositions $NbGe_{0.67\pm0.05}$, $NbGe_{0.54\pm0.06}$ and Nb_3Ge in addition to $NbGe_2$, which had previously been reported. The decomposition temperature of $NbGe_2$ is 1483 ± 15°. The $NbGe_{0.67}$ compound is stable at least to 1650° and $NbGe_{0.54}$, and Nb_3Ge are stable at least to 1910 ± 15°. Nb_3Ge has the β-tungsten structure, with $a = 5.168 \pm 0.002$ Å. $NbGe_2$ belongs to the space group $D_6^4 - P6_222$ or $D_6^5 - P6_422$ with $a = 4.966 \pm 0.003$ Å. and $c = 6.781 \pm 0.003$ Å. Reactivities of the niobium germanides toward some common chemicals are reported.

The unusual high temperature stability, strength and chemical inertness of the transition metal carbides and silicides have stimulated much research on these compounds. Although the transition metal germanides are chemically and physically similar, little research has been conducted on their structures, preparations and properties. In this paper, the compositions and some of the properties of the niobium germanides are reported. The only previous reference in the literature to a niobium germanide is a statement by Wallbaum of the structure type and lattice constants of $NbGe_2$.[3]

Composition Studies

Experimental.—Each sample was prepared by mixing weighed amounts of niobium and germanium powders, heating the mixture *in vacuo* for the length of time necessary to reach phase equilibrium, cooling and examining the product by X-ray diffraction techniques for the phases present.

Niobium was purchased from the Fairmont Chemical Company as 200 mesh powder. Analysis showed the powder to be 99.4% pure with the major impurities being carbon and tantalum.

Germanium was obtained from the Eagle–Picher Company. This germanium was 99.9% pure with respect to spectroscopically detectable impurities but contained a considerable amount of germanium oxide which was expelled by heating *in vacuo* before the germanium was used.

Details of apparatus and techniques used in preparing samples, in establishing compositions of compounds produced[4,5] and in quenching samples[6,7] are described elsewhere.

Results and Discussion.—Twenty-six preparations were made in graphite crucibles and were cooled at initial rates of about 300° per minute. Preparations heated at 1100° for 39 minutes usually failed to reach equilibrium; lines of the phase established by Wallbaum as $NbGe_2$ appeared in all patterns regardless of compositions. In some samples of relatively high niobium content only $NbGe_2$ lines could be detected by use of copper Kα X-radiation even though unreacted niobium must have been present. Behavior of niobium–germanium samples heated at higher temperatures and the known behavior of chemically related compounds make clear that $NbGe_2$ was formed readily and coated unreacted niobium grains. Compounds of intermediate compositions must have been present as intermediate layers too thin to give detectable diffraction patterns. Growth of these layers could then proceed only by slow diffusion.

Samples heated in graphite to 1400° for 30 minutes or to 1600° for 60 minutes showed formation of three niobium germanide compounds. X-Ray photographs revealed the presence of NbC in those samples heated at 1600° for which the germanium content was greater than 50 mole %. Preparations heated at 1400° for 30 minutes showed no indications that equilibrium was not reached or that crucible attack had occurred; however, attempts to determine from composition *versus* diffraction studies the composition of $NbGe_2$ (known from X-ray data) resulted in the appearance of free germanium in samples of germanium content greater than $NbGe_{1.82}$, indicating that some crucible attack had taken place.

To obtain more accurate determinations of compositions and to prove that graphite was not needed to stabilize the compounds observed, 26 samples of various compositions were prepared in tungsten crucibles at 1400°. The same niobium germanide phases were observed. From examination of the diffraction patterns, compound composition limits were fixed as $NbGe_{0.60} \pm 0.05$, $NbGe_{0.67} \pm 0.05$ and $NbGe_{2.0} \pm 0.3$. The uncertainties in compositions arise from difficulty in detecting from the diffraction photographs one phase in the presence of an excess of another phase.

Variation in dissociation pressures with composition at constant temperature[7] indicated the compositions of the two phases to be $NbGe_{0.58} \pm 0.03$ and $NbGe_{0.68} \pm 0.03$. From considerations of all the data, the compositions of the two phases are believed to be $NbGe_{0.54} \pm 0.06$ and $NbGe_{0.67} \pm 0.05$. The uncertainties include the extremities of composition believed consistent with the data.

The crystal structures of $NbGe_{0.54}$ and of $NbGe_{0.67}$ have been determined by Nowotny, Searcy and Orr.[8] Both compounds crystallize with structures for which the ideal composition is Nb_5Ge_3; however, there can be no doubt that the niobium contents are different in the two phases. Furthermore, evidence is strong that some of the silicides that crystallize with M_5Si_3 ideal structures have compositions closer to M_3Si_2 ($MSi_{0.67}$) than M_5Si_3 ($MSi_{0.60}$) in complete analogy with the $NbGe_{0.67}$ phase found in this work. Thus, like the wüstite phase of the iron–oxygen system, these two germanides apparently crystallize with defect structures so that no

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[1] Based on a thesis submitted by John H. Carpenter in partial fulfillment of the requirements for the Ph.D. degree at Purdue University.

[2] Supported by the Office of Naval Research.

[3] H. J. Wallbaum, *Naturwissenschaften*, **32**, 76 (1944).

[4] A. W. Searcy and R. A. McNees, Jr., THIS JOURNAL, **75**, 1578 (1953).

[5] A. W. Searcy and R. J. Peavler, *ibid.*, **75**, 5657 (1953).

[6] J. H. Carpenter, M.S. Thesis, Purdue University, August, 1953.

[7] J. H. Carpenter, Ph.D. Thesis, August, 1955.

[8] H. Nowotny, A. W. Searcy and J. E. Orr, *J. Phys. Chem.*, **60**, 677 (1956).

simple chemical formula can properly be assigned them. The $NbGe_{0.67}$ compound dissolves carbon[8] and may require carbon or oxygen for its existence. However, it was prepared with less than 0.5% carbon so that its existence in the binary niobium–germanium system is probable.

A fourth niobium germanide compound was first detected in samples quenched from above 1800°. The composition of this compound could not be established from diffraction studies in the same ways as were compositions of the other compounds because at the temperatures of its formation, niobium soaked into the tungsten crucibles changing the composition of the samples. The compound was identified as Nb_3Ge by structure studies described in a later section of this paper.

Formation of Nb_3Ge occurs slowly from $NbGe_{0.54}$ and niobium. More than 3 hr. of heating at 1700° are required to establish equilibrium. The compound may be unstable at lower temperatures; more probably it simply forms too slowly below 1700° to detect after only a few hours heating.

Table I lists the results of quenching experiments for samples with compositions near $NbGe_2$. These samples showed three phases when quenched from 1493° or above but only one or two phases when quenched from 1472° or lower. It can be concluded that $NbGe_2$ disproportionated at 1483 ± 15°. Spacings of lines for the third phase, or phases, in samples quenched from above 1483° agree with those for the higher niobium content compounds, but the lines are too weak for positive identification.

TABLE I

QUENCHING DATA FOR $NbGe_2$

Atomic ratios Nb:Ge (before heating)	Quenching temp., (°C.)	Heating period (min.)	Phases present[a]	Crucible material
0.42	1216	30	*$NbGe_2$*, Ge	C
$NbGe_2$ + Ge reheated	1273	1200	$NbGe_2$, Ge	C
0.54	1472	120	$NbGe_2$	W
.30	1493	20	*$NbGe_2$, Ge ?*	W
.42	1584	30	*$NbGe_2$, Ge ?*	C

[a] Italic phases gave the stronger X-ray patterns.

Quenching data for $NbGe_{0.67}$ showed no evidence for decomposition at temperatures up to 1646°, the highest temperature investigated. Neither $NbGe_{0.54}$ nor Nb_3Ge showed evidence of decomposition at temperatures up to 1938°; however, samples of compositions between $NbGe_{0.54}$ and Nb_3Ge were observed to melt at 1910 ± 15°.

Crystal Structures

Experimental Measurements.—For all X-ray work, nickel filtered copper Kα radiation was used (wave lengths α_1 = 1.54052 Å. and α_2 = 1.54437 Å.). Data were obtained from both X-ray powder diffraction photographs and Geiger counter diffractometer traces. When 2θ values were obtained from films, a film shrinkage correction was applied. Intensities were obtained from films by visual estimation.

Results and Discussion.—Wallbaum[3] reported $NbGe_2$ to have the $CrSi_2$ structure, but apparently no details of his analysis have been published. Hence, a determination of the crystal structure of $NbGe_2$ was undertaken. The average hexagonal lattice constants found were a = 4.966 ± 0.003 Å. and c = 6.781 ± 0.003 Å. (c/a = 1.365) compared to a = 4.957 and c = 6.770 reported by Wallbaum.

The density of a fused sample of $NbGe_2$ was found to be 7.81 ± 0.24 g./ml. by water and CCl_4 displacement. Three molecules of $NbGe_2$ per unit cell correspond to a theoretical density of 8.20 g./ml.

Reflections of the type 00l were observed only if $l = 3n$ and reflections for which $h = 2n$ and $k = 2n$ were observed only if $l = 3n$. Possible space groups for these extinctions are C^4–$P6_2$, C_6^5–$P6_4$,

TABLE II

CRYSTALLOGRAPHIC DATA FOR $NbGe_2$

hkl	d(Å.)	Sin² θ		Intensity	
		Obsd.	Calcd.	Visual[c]	Calcd.
101	3.632	0.0451	0.0450	vw⁻	1
102	2.666	.0835	.0838	vw⁻	1
110	2.482	.0964	.0964	m	15
111	2.331	.1093	.1093	vs⁺	100
003	2.260	.1163	.1163	s	35
200			.1285		0.5
112	2.003	.1482	.1481	vs	63
103			.1484		0.09
113	1.671	.2126	.2127	m⁻	9
210			.2249		0.04
211			.2378		0.3
104			.2389		0.1
203			.2448		0.3
212			.2766		0.2
300	1.429	.2895	.2892	vw	2
114)	1.401	.3027	.3032	s	37
301)			.3021		
302	1.321	.3408	.3409	m	15
213			.3412		0.04
105			.3552		0.07
220	1.241	.3856	.3856	m	14
303	1.209	.4051	.4055	vw	3
310			.4177		0.02
115	1.191	.4192	.4195	m	11
311			.4306		0.1
214			.4317		0.1
006	1.130	.4655	.4653	vw	3
312			.4694		0.1
304	1.095	.4955	.4960	m⁻	9
106			.4974		0.01
223	1.088	.5019	.5019	m	12
400			.5141		0.06
313			.5340		0.03
215			.5480		0.1
116	1.028	.5615	.5616	vw	2
206			.5938		0.1
320			.6105		0.01
305	0.9850	.6115	.6113[a]	w	7
321			.6224[a]		0.1
403			.6294[a]		0.1
322			.6611[a]		0.1
107			.6643[a]		0.06
410	.9386	.6746	.6736[a]	vw	2
411	.9297	.6863	.6865[a]	m	14
216			.6890[a]		0.03
412	.9045	.7251	.7252[a]	m⁻	9.5[a]
323			.7256[a]		0.03
412	.9045)	.7287	.7289[b]	m⁻	9.5
117	.9023)		.7285[a]		

[a] Value for CuKα_1 radiation. [b] Value for CuKα_2 radiation. [c] s, strong; m, medium; w, weak; v, very.

D_6^4–$P6_222$ and D_6^5–$P6_422$. Of these space groups the first two and the latter two result in enantiomorphic pairs of identical structures. Enantiomorphic structures are indistinguishable by the powder methods used. Choosing a space group with the higher symmetry, all calculations were performed on D_6^4–$P6_222$. Satisfactory agreement with experiment was obtained.

Relative intensities were calculated from the relation

$$I_o = \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}\, p\, |F_{hkl}|^2 K$$

where θ is the Bragg angle, p is the multiplicity, F_{hkl} is the structure factor and K is a proportionality constant.

Crystallographic data for $NbGe_2$ are shown in Table II. Atoms are in the following positions, 3 Nb in (d): $^1/_2, 0, ^1/_2;\ 0, ^1/_2, ^1/_6;\ ^1/_2, ^1/_2, ^5/_6$ and 6 Ge in (j): $x, 2x, ^1/_2;\ 2\bar{x}, \bar{x}, ^1/_2;\ x, \bar{x}, ^5/_6;\ \bar{x}, 2\bar{x}, ^1/_2;\ 2x, x, ^1/_6;\ \bar{x}, x, ^5/_6$. The value $^1/_6$ was chosen for x. No attempt was made to refine the parameter.

Each niobium atom in $NbGe_2$ has four germanium atoms at 2.68 Å., six germanium atoms at 2.87 Å. and four niobium atoms at 3.36 Å. Each germanium atom is surrounded by two germanium and two niobium atoms at 2.68 Å., three germanium and three niobium atoms at 2.87 Å. and four germanium atoms at 3.36 Å.

A diffraction pattern of Nb_3Ge corresponds very closely in both spacings and intensities to the patterns of Mo_3Ge[9] and Mo_3Si[10] which have the cubic "β-tungsten" structure. For Nb_3Ge the lattice constant is $a = 5.168 \pm 0.002$ Å. Water displacement yielded a density of 8.17 g./ml. The theoretical density is 8.47 g./ml. assuming two molecules of Nb_3Ge per unit cell.

Calculated intensities agree well with the observed intensities and consequently fix the space group for Nb_3Ge as O_h^3–Pm3n with atoms in the positions 2 Ge in (a): $0, 0, 0;\ ^1/_2, ^1/_2, ^1/_2$ and 6 Nb in (c): $^1/_4, 0, ^1/_2;\ ^1/_2, ^1/_4, 0;\ ^3/_4, 0, ^1/_2;\ 0, ^1/_2, ^1/_4;\ ^1/_2, ^3/_4, 0;\ 0, ^1/_2, ^3/_4$. Each germanium atom in Nb_3Ge is surrounded by 12 niobium atoms at a distance of 2.89 Å. Each niobium atom has two niobium atoms at 2.58 Å., four germanium atoms at 2.89 Å. and eight niobium atoms at 3.17 Å.

Chemical Properties

The niobium germanides were tested for reactivity with a variety of common chemicals. Solutions were placed in contact with the germanides overnight and then were heated. All the compounds reacted readily with fused sodium carbonate and fused sodium hydroxide. All reacted with hydrofluoric acid (48%), hydrogen peroxide solution (30%) and sodium hydroxide solutions in the cold. Only $NbGe_{0.64}$ failed to react with concentrated hydrochloric acid. Concentrated sulfuric acid reacted with $NbGe_2$ and Nb_3Ge when hot after failing to react cold. All the niobium germanides were unreactive toward concentrated hydriodic acid, nitric acid (concentrated or dilute), 6 *N* sulfuric acid, dilute hydrochloric acid and aqua regia. The niobium germanides react with more of these reagents than do molybdenum germanides[5] and tantalum germanides,[11] although the niobium germanides are thermodynamically more stable.[7]

Acknowledgment.—We are greatly indebted to Professor Hans Nowotny for discussions of the phase composition data.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Equilibria in Alkaline Argentocyanide Solutions

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In the presence of strong alkali, silver and argentocyanide ions react according to $Ag^+ + 20H^- + Ag(CN)_2^- \rightleftarrows 2Ag\left\{\begin{matrix}(OH)\\(CN)\end{matrix}\right.^-$. At 25° the formation constant $K_A = \left[Ag\left\{\begin{matrix}(OH)\\(CN)\end{matrix}\right.^-\right]^2/[Ag^+][OH^-]^2[Ag(CN)_2^-] = 3.4 \pm 0.8 \times 10^6$. The instability constant of the hydroxyargentocyanide ion $K_{Hy} = [Ag^+][OH^-][CN^-]/\left[Ag\left\{\begin{matrix}(OH)\\(CN)\end{matrix}\right.^-\right] = 6 \times 10^{-14}$. The solubility product of silver cyanide is calculated as $2.3 \pm 1 \times 10^{-16}$.

In an examination of the mechanism of the amperometric argentometric titration of cyanide in sodium hydroxide medium,[1] we observed that argentocyanide greatly increases the solubility of silver hydroxide and of silver cyanide. In the present paper it is shown that this effect is due to the reaction

$$Ag^+ + 2OH^- + Ag(CN)_2^- \rightleftarrows 2Ag\left\{\begin{matrix}(OH)\\(CN)\end{matrix}\right.^- \quad (A)$$

We have determined the equilibrium constant K_A of this reaction and have also obtained a value for the solubility product of silver cyanide.

Experimental

C.P. reagents and conductivity water were used in the preparation of all solutions. Apart from the data shown in Table IV and in Figs. 2 and 3, which were obtained with air-containing solutions at room temperature (approximate range 22 to 25°), all observations refer to solutions at 25.0 ± 0.1° which were deoxygenated by means of a stream of nitrogen.

The approximately 0.2 *M* potassium cyanide stock solution was standardized daily.[2] Portions of the stock solution were diluted as required with sodium hydroxide solution. Potassium argentocyanide solutions were prepared as needed by mixing the calculated volumes of potassium

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[1] H. A. Laitinen, W. P. Jennings and T. D. Parks, *Ind. Eng. Chem., Anal. Ed.*, **18**, 574 (1946).

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