Acta Cryst. (1982). B38, 917–918

Nickel Scandium Germanide $Sc_3Ni_4Ge_4$: A New Ternary Germanide with the $Gd_6Cu_8Ge_8$-Type Structure

BY B. YA. KOTUR* AND M. SIKIRICA

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, PO Box 153, 41001 *Zagreb, Yugoslavia*

(*Received* 11 *May* 1981; *accepted* 25 *September* 1981)

Abstract. $Sc_3Ni_4Ge_4$, orthorhombic, *Immm*, $Z = 2$, $a = 12{\cdot}910\ (9)$, $b = 6{\cdot}598\ (4)$, $c = 3{\cdot}908\ (2)$ Å, $V = 332{\cdot}88$ Å^3, $\mu = 31{\cdot}1$ mm^{-1} (Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}7107$ Å). The compound crystallizes with the $Gd_6Cu_8Ge_8$-type structure. The structure was refined from single-crystal data. The final $R = 0{\cdot}042$ for 205 reflections with isotropic thermal parameters for all atoms.

Introduction. During the investigation of the Sc–Ni–Ge system, among several new ternary germanides, a compound with the approximate composition $Sc_3Ni_4Ge_4$ was found. Its powder diffractogram was very similar to that of $Sc_3Ni_4Si_4$ (Bodak, Kotur & Gladyshevsky, 1976), the crystal structure of which was reported to be of the $Gd_6Cu_8Ge_8$ type (Rieger, 1970). As the crystal structure of $Sc_3Ni_4Si_4$ had been determined from powder data and the atomic parameters had not been refined, we decided to perform a full structure investigation of $Sc_3Ni_4Ge_4$ from single-crystal data.

A single crystal of prismatic shape with dimensions $0{\cdot}024 \times 0{\cdot}008 \times 0{\cdot}066$ mm was isolated from a crushed ingot of stoichiometry close to $Sc_3Ni_4Ge_4$. The sample was prepared by arc melting. The single crystal was examined by Laue and rotation photographs. The Laue class *mmm* and the systematic absences (*hkl* with $h + k + l = 2n$, *hk*0 with $h + k = 2n$, *h*0*l* with $h + l = 2n$, 0*kl* with $k + l = 2n$, *h*00 with $h = 2n$, 0*k*0 with $k = 2n$, 00*l* with $l = 2n$) indicate *Immm*, *Imm*2, *I*222 and $I2_12_12_1$ as the possible space groups. The space-group symmetry together with the lattice parameters indicated the $Gd_6Cu_8Ge_8$-type structure.

Intensity data were collected by means of a Philips PW 1100 four-circle diffractometer (graphite-monochromatized Mo $K\bar{\alpha}$ radiation). Integrated intensities of 205 reflections were collected in the θ–2θ scan mode up to a limit of $\sin\theta/\lambda = 0{\cdot}70$ Å^{-1}. Lattice parameters (see *Abstract*) were obtained from the 2θ values for 13 reflections by means of the least-squares method.

The parameters of $Gd_6Cu_8Ge_8$ given by Rieger (1970) were used as starting values for a least-squares refinement with the program *SYST* (Domenicano, Spagna & Vaciago, 1969). Corrections for Lorentz–polarization effects and for absorption were made. The atomic scattering factors were those of Cromer & Mann (1968) with corrections for anomalous scattering from Cromer & Liberman (1970). The final $R = \sum |\Delta F| / \sum F_o$ was 0·042.*

The final atomic parameters are given in Table 1 and interatomic distances in Table 2.

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36436 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional* ($\times 10^4$) *and isotropic thermal parameters for* $Sc_3Ni_4Ge_4$

E.s.d.'s are given in parentheses.

		x	y	z	B_{iso} (Å^2)
Sc(1)	2(*d*)	0	½	0	0·564 (6)
Sc(2)	4(*e*)	1266 (3)	0	0	0·35 (4)
Ni	8(*n*)	3231 (2)	1960 (3)	0	0·39 (3)
Ge(1)	4(*f*)	2189 (2)	½	0	0·373 (5)
Ge(2)	4(*h*)	0	1941 (4)	½	0·32 (4)

Table 2. *Interatomic distances* (Å) *in* $Sc_3Ni_4Ge_4$

E.s.d.'s are given in parentheses.

Sc(1)–4Sc(2)	3·682 (3)	Ni–2Sc(1)	3·272 (2)
8Ni	3·272 (2)	2Sc(2)	2·875 (4)
2Ge(1)	2·826 (3)	Sc(2)	2·847 (5)
4Ge(2)	2·809 (2)	2Ni	2·809 (3)
		Ni	2·586 (3)
Sc(2)–2Sc(1)	3·682 (3)	Ge(1)	2·415 (3)
2Ge(1)	3·508 (3)	2Ge(1)	2·405 (2)
Sc(2)	3·269 (6)	Ge(2)	2·396 (3)
4Ni	2·875 (4)		
4Ge(2)	2·851 (3)	Ge(1)–2Sc(2)	3·508 (3)
2Ni	2·847 (5)	Sc(1)	2·826 (3)
2Ge(1)	2·792 (4)	2Sc(2)	2·792 (4)
		2Ni	2·415 (3)
		4Ni	2·405 (2)
		Ge(2)–4Sc(2)	2·851 (3)
		2Sc(1)	2·809 (2)
		Ge(2)	2·561 (4)
		2Ni	2·396 (3)

* Permanent address: Chair of Inorganic Chemistry, University of Lvov, Lomonosov Street 6, 290005 Lvov, USSR.

0567-7408/82/030917-02$01.00

Discussion. $Sc_3Ni_4Ge_4$ is a new representative of a family of $Gd_6Cu_8Ge_8$-type structure phases. The compounds with this structure were found previously in the ternary systems R–Cu–Si(Ge) (R = rare-earth metal, REM) (Rieger, 1970; Hanel & Nowotny, 1970) and Zr(Hf)–Cu–Si (Springer, 1974). The radius of the largest atom in these compounds varies in the range 1·80 (Sm) to 1·59 (Hf) Å. The same is true for the $ThCu_2Si_2$ (Ban & Sikirica, 1965) and TiNiSi (Shoemaker & Shoemaker, 1965) structure types. This is why families of compounds with these three types of structure are numerous. The phases with the $ThCu_2Si_2$ and TiNiSi structure types are very often in equilibrium with the phase with $Gd_6Cu_8Ge_8$ type; they are its nearest neighbours. The compositions of these phases in the ternary systems R–T–T' (R = REM, Zr, Hf; T = 3d transition metal; T' = Si, Ge) lie on the section with a T-to-T' atomic ratio of 1:1. At least one of the lattice parameters of these structures is ~4 Å, which is the height of the trigonal prism which forms the coordination polyhedron around the T' atoms. Three kinds of trigonal prisms can be found in these structures: $[T'R_6]$, $[T'R_4T_2]$ and $[T'R_2T_4]$. The connections of the prisms in these structures are presented in Fig. 1. In some REM-containing systems (except Sc) the $Gd_6Cu_8Ge_8$-type phases are in equilibrium with the phases of the AlB_2 type (Rieger, 1970). This is not surprising, since the former also contain fragments of the latter (see Fig. 1).

Thus on the section with atomic ratio $T:T' = 1:1$, the change of the R-atom content leads to a change in the crystal structure of the phases. The known factors which govern the occurrence and crystal structure of intermetallics are atomic size, electron concentration, electronegativity, *etc.* (Pearson, 1972). However, there are no quantitive methods, based on the factors mentioned above, which allow the theoretical calculation of the compositions and crystal structures of intermetallics. But it can be seen that the phases which lie on the same sections, defined by the atomic ratios $R:T$, $R:T'$, $T:T'$ *etc.*, have interconnected structures (for one another, *e.g.* of the Sc:Si = 1:1 section in the Sc–Co–Si system, see Gladyshevsky & Kotur, 1978). In this way the search for geometric relationships among the structures may facilitate the investigation of the unknown structures.

The authors thank Mr R. I. Andrusyak for assistance in the preparation of the samples and Mr M. Bruvo for the diffractometer-data collection.

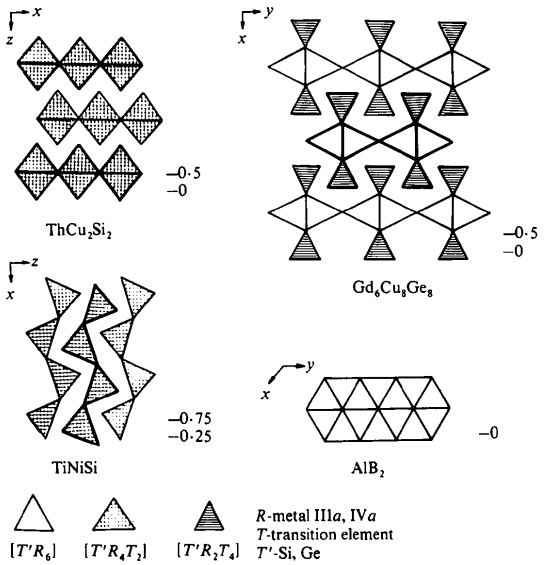

Fig. 1. Connections of trigonal prisms $[T'R_6]$, $[T'R_4T_2]$ and $[T'R_2T_4]$ in the structures isotypic with $ThCu_2Si_2$, $Gd_6Cu_8Ge_8$, TiNiSi and AlB_2.

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