

SUPERCONDUCTIVITY IN TERNARY RARE EARTH-TRANSITION METAL SILICIDES: A CRITICAL REVIEW

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Summary

Ternary rare earth-transition metal silicides crystallize with a multitude of structure types. The occurrence of superconductivity among these compounds is critically examined, and their crystallography and magnetic and transport properties are discussed. New data on the ternary system La-Rh-Si are also presented.

1. Introduction

The remarkable properties of ternary compounds are a subject of continuing intense research interest. In the field of superconductivity, considerable impetus has been provided by two classes of compounds, the Chevrel phases MMo_6X_8 [1], where X is a chalcogen and M can be any of a large number of metal atoms, including rare earths, and the borides MRh_4B_4 [2], where M can be yttrium, thorium or a lanthanide atom. In both classes, superconductivity may occur even when M is a magnetic rare earth element, and these materials containing an ordered rare earth sublattice have provided the first opportunities to explore the interaction between superconductivity and long-range magnetic ordering. In addition, the molybdenum chalcogenides have the highest upper critical fields ever observed and are of interest for technical applications.

These unique properties stimulated the synthesis of other ternary systems, *e.g.* the stannides [3], phosphides [4] and silicides [5, 6]. An introduction into the research on ternary superconductors and comprehensive reviews of the literature up to 1982 may be found in refs. 7 - 10.

The number of ternary silicide systems containing superconducting compounds has rapidly evolved since, and it is the purpose of this paper to give a critical review of this field, proceeding in a systematic manner by structure class. Only true ternary compounds in a crystallographic sense, *i.e.* containing three elements, each occupying a distinct set or sets of crystallographic sites, will be considered.

In the following sections, we shall present the structure classes treated in this review and bring up some of the experimental difficulties encountered in ternary superconductors (Section 2), discuss the crystallography of each class and review the superconductivity and magnetism of its members (Sections 3.1 - 3.8), briefly survey non-superconducting phases in ternary systems containing also superconducting phases (Section 4) and attempt to point out general trends and structural relationships among superconducting silicides (Section 5).

This review cannot give a complete introduction to ternary silicides in general, simply because of the sheer numbers of known structure types. The reader is referred to the review by Parthé and Chabot [11] as a source of inspiration.

2. Superconducting ternary silicides

While the Chevrel phases and rhodium borides accept a large variety of ternary constituent M, in keeping their basic structure, characterized by octahedral Mo_6 clusters and Rh_4 tetrahedra respectively, the silicides exhibit a large diversity of crystallographic structures, with little tolerance for replacement of one of the constituents. Research has focused mainly on compounds $\text{M}_x\text{T}_y\text{Si}_z$ where M is a rare earth and T a transition metal of the iron or platinum groups. In part, this choice was made in the hope of finding new examples for interactions between superconductivity and magnetism, but it may also reflect the fact that these systems contain large numbers of ternary phases and thus offer good opportunities for the discovery of new superconductors. The basis set of structure classes treated in this review is listed in Table 1. For each structure class, one representative isotypic superconducting compound and its superconducting transition temperature T_c are given.

The structure types have been determined by single-crystal X-ray diffraction, with the exception of the LaRu_3Si_2 type, which has been determined from X-ray powder data. In general, the isotypic compounds were identified using X-ray powder diffraction at room temperature. Only a few compounds have been tested for a low temperature structural phase transformation. Such transformations may cause unexpected low temperature behaviour, as has been shown for Chevrel phase compounds [31].

As has been pointed out [32], the most studied binary structure classes, A15 and B1, are characterized by the fact that the atomic positions are fixed with respect to the unit cell edges. In most ternary structure classes exhibiting interesting properties, the atomic positions are variable with respect to the unit cell axes so that *a priori* unpredictable electronic and lattice properties can result while the same structure and similar lattice parameters are retained on change in composition. Thus, any serious discussion of structure-dependent properties, *e.g.* band structure or crystalline electric field, should be based on accurate structure determination on single crystals of the compound under consideration, preferably done at low temperature.

TABLE 1
Structure types of superconducting ternary silicides

| <i>Compound</i> | T_c (K) | <i>Reference</i> | <i>Structure type</i> | <i>Space group</i> | <i>Z</i> | <i>Reference</i> |
|---|--------------|------------------|--|-------------------------|----------|------------------|
| Sc ₅ Ir ₄ Si ₁₀ | 8.4 | [6] | Sc ₅ Co ₄ Si ₁₀ | <i>P4/mbm</i> | 2 | [12] |
| LaRu ₃ Si ₂ | 7.3 | [13] | LaRu ₃ Si ₂ | <i>P6₃22</i> | 2 | [14] |
| Lu ₂ Fe ₃ Si ₅ | 6.0 | [15] | Sc ₂ Fe ₃ Si ₅ | <i>P4/mnc</i> | 4 | [16] |
| La ₂ Rh ₃ Si ₅ | 4.4 | [17] | U ₂ Co ₃ Si ₅ | <i>Ibam</i> | 4 | [18] |
| LaPtSi | 3.5 | [19] | LaPtSi | <i>I4₁md</i> | 4 | [20] |
| LaRhSi ₂ | 3.4 | [21] | CeNiSi ₂ | <i>Cmcm</i> | 4 | [22] |
| LaRhSi ₃ | 2.3 | [23, 24] | BaNiSn ₃ | <i>I4mm</i> | 2 | [25] |
| LaIr ₂ Si ₂ | 1.6 | [26] | CaBe ₂ Ge ₂ | <i>P4/nmm</i> | 2 | [27] |
| CeCu ₂ Si ₂ | 0.6 | [28] | ThCr ₂ Si ₂ | <i>I4/mmm</i> | 2 | [29] |
| La ₃ Rh _{≈1} Si _{≈1} | 4.4 | [23] | Unknown | Tetragonal | | [30] |
| Sc ₄ RhSi _{≈8} | 1.8 | [6] | Unknown | ? | | |

Another experimental complication has to do with the complexity of the ternary phase diagrams involved. While in a binary system, at given temperature and pressure, each phase may be in equilibrium with two neighbouring phases at most, this number may be large in ternary systems. Frequently it is difficult to obtain truly single-phase specimens of a ternary phase because of their narrow homogeneity ranges and long equilibration times. Thus, to prove that a certain physical property is intrinsic to a given phase (or rather that it is not due to an impurity), it may be necessary to test a considerable number of neighbouring phases in a ternary system.

Some of the ternary silicide systems contain more than one superconducting phase (Table 1). To illustrate this point further, two compounds were included at the bottom of Table 1, even though their structure and exact composition are not known yet.

The claim of superconductivity for a given compound should ideally be based on bulk measurements: specific heat or d.c. Meissner effect. Both methods are not suited for a rapid survey of a large number of compounds. To a good approximation, measuring the a.c. susceptibility on bulk pieces and powder, ground to less than the grain size (and possibly strain relief annealed), will establish whether superconductivity is a true property of the bulk of the specimen under study or is spurious and due to impurity phases. For obvious reasons, resistivity measurements alone cannot prove the existence of bulk superconductivity in a sample.

However, the failure to find superconductivity in one sample of a given phase does not constitute proof that this phase cannot be superconducting; the phase may have a homogeneity range and the superconducting properties may strongly depend on the actual composition of the specimen. Further, the homogeneity range may vary with temperature. These peculiarities of phase diagrams are encountered in A15 compounds and are well understood. A discussion is given in the review by Muller [33] (for recent references see Junod *et al.* [34]).

3. Crystallography, superconductivity and magnetism of superconducting ternary silicides

3.1. Primitive tetragonal $Sc_5Co_4Si_{10}$ structure

The structure of $Sc_5Co_4Si_{10}$ (and of $Sc_5Ir_4Si_{10}$) has been determined on single crystals [12]. As shown in Fig. 1, the cobalt and silicon atoms form planar nets of hexagons and pentagons which are connected along the [001] direction via Co–Si–Co zigzag chains to form a three-dimensional network with short Co–Si distances ($d_{Co-Si} = 2.2 - 2.35 \text{ \AA}$ [12]). The transition metal (cobalt) atoms are isolated from each other. Each cobalt has five silicon neighbours at the apex of a (distorted) square pyramid. A similar pyramid pointing in the opposite direction, its base turned 45° , is made up by the five scandium neighbours of cobalt. The two basal planes of the silicon and scandium pyramids form a (distorted) square antiprism, whose rectangular faces are capped by the remaining silicon and scandium atoms respectively. This coordination polyhedron is the building block characteristic of $BaAl_4$ -derived structures (see Section 3.8) and is frequently found in binary and ternary silicide compounds, transition metal and silicon atoms sometimes interchanging sites [11, 35]. Each silicon atom has two cobalt nearest neighbours, and Si forms Si–Si pairs ($d_{Si-Si} = 2.30 - 2.45 \text{ \AA}$ [12]).

$Sc_5Co_4Si_{10}$ -type silicides and germanides of stoichiometry $M_5T_4X_{10}$ form with a range of transition metals and trivalent M atoms. Seven compounds with $M \equiv Sc, Y, Lu$ and $T \equiv Co, Rh, Ir, Os$ exhibit superconductivity, three of them between 8 and 9 K [6, 36]. At least one of these compounds, $Sc_5Rh_4Si_{10}$, is stable only above 950°C [5], and has to be quenched from above this temperature to study its low temperature properties. $Sc_5Co_4Si_{10}$ and $Sc_5Ir_4Si_{10}$ exhibit metallic behaviour with resistance ratios of about 10, negative curvature of the resistance *versus* temperature dependence above 70 K and residual resistivities of about $10 \mu\Omega \text{ cm}$ [36]. Suscep-

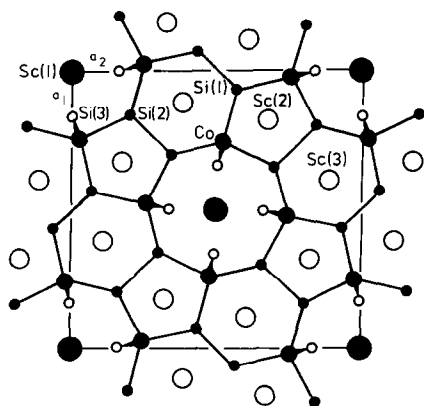


Fig. 1. Projection of the $Sc_5Co_4Si_{10}$ structure along the [001] direction (the Co–Si net is outlined by bold lines): ●, scandium ($z = 0$); ○, scandium ($z = \pm 1/2$); ●, cobalt ($z = 0$); ●, silicon ($z = 0$); ○, silicon ($z = \pm 1/2$). (After Braun *et al.* [12].)

tibility measurements indicate that the cobalt atoms do not carry local magnetic moment [36]. The susceptibilities of the superconducting compounds are temperature independent and fairly low, between 28×10^{-6} e.m.u. (g atom) $^{-1}$ for $\text{Sc}_5\text{Co}_4\text{Si}_{10}$ and 1.3×10^{-6} e.m.u. (g atom) $^{-1}$ for $\text{Lu}_5\text{Ir}_4\text{Si}_{10}$; $\text{Y}_5\text{Ir}_4\text{Si}_{10}$ is weakly diamagnetic (-2.2×10^{-6} e.m.u. (g atom) $^{-1}$) [36, 37].

Compounds containing a rare earth ion with an incomplete 4f shell show magnetic ordering at low temperatures of the antiferromagnetic type (judged from the cusp in d.c. susceptibility and linear magnetization curves) [37]. At higher temperatures, the susceptibilities follow a Curie-Weiss law, with effective moments consistent with trivalent rare earth ions in a Hund's rule ground state [37].

3.2. Hexagonal LaRu_3Si_2 structure

The structure of LaRu_3Si_2 was determined from X-ray powder diffraction data by Vandenberg and Barz [14]. This structure may be considered a distorted derivative of the CeCo_3B_2 -type structure [38], which is an ordered ternary variant derived from the CaCu_5 type [39]. A comprehensive list of the known CaCu_5 -type derivatives is given by Parthé and Chabot [11]. An overview of superconducting borides with closely related structures may be found in ref. 32.

The lanthanum atoms form a simple hexagonal lattice as in the CeCo_3B_2 structure. The T metal sublattice becomes distorted in such a way that larger and smaller triangular clusters are formed. In LaRu_3Si_2 , the Ru-Ru distance within a small triangle is 2.76 Å; the distance between these is 2.93 Å. The interlayer Ru-Ru distance is no longer metallic (3.57 Å) [14]. Superconductivity is observed for the lanthanum ($T_c = 7.3$ K), yttrium ($T_c = 3.5$ K) and thorium ($T_c = 3.9$ K) compounds, while magnetic ordering was found for most of the remaining LaRu_3Si_2 -type compounds containing magnetic rare earths [13].

Non-superconducting silicides MRh_3Si_2 with the CeCo_3B_2 -type structure (powder data) were reported by Chevalier *et al.* [40]. The compounds with yttrium and lanthanum are diamagnetic with susceptibilities of -17.8×10^{-6} e.m.u. (g atom) $^{-1}$ and -8.3×10^{-6} e.m.u. (g atom) $^{-1}$ at 300 K respectively. For compounds with Nd-Er, (ferro)magnetic ordering is reported, with the highest Curie temperature of 37 K for TbRh_3Si_2 and free-ion effective moments in the paramagnetic state [40].

3.3. Primitive tetragonal $\text{Sc}_2\text{Fe}_3\text{Si}_5$ -type compounds

The compounds of this structure class are unusual in several aspects. Members of this class exhibit the highest superconducting transition temperatures known for iron-containing compounds, and this is the only class of silicides, apart from CeCu_2Si_2 , showing superconductivity in a compound containing a rare earth element with an incomplete 4f shell.

The structure types of $\text{Sc}_2\text{Fe}_3\text{Si}_5$ [16], $\text{U}_2\text{Co}_3\text{Si}_5$ [18], BaNiSn_3 [27], CaBe_2Ge_2 [25] and ThCr_2Si_2 [29, 41] are closely related and can be derived

approximately equal (2.64 and 2.67 Å), while the nearest distance between the different sets is considerably larger (4.10 Å) [15]. Thus, the transition metal in this class of compounds forms two types of clusters, although not in the most stringent sense since the Fe-Fe intracluster distances are larger than in iron metal (2.48 Å) [35]. Fe(1) is octahedrally and Fe(2) is tetrahedrally surrounded by silicon atoms ($d_{\text{Fe-Si}} = 2.28 - 2.57$ Å [35]). The Fe(1) squares alternate with scandium squares along the [001] direction, forming (distorted) square antiprisms centred by silicon. The rare earth nearest-neighbour distance is 3.70 Å in $\text{Sc}_2\text{Fe}_3\text{Si}_5$.

The iron-based compounds with $M \equiv \text{Sc}$ ($T_c = 4.5$ K), Y ($T_c = 2.2$ K), Lu ($T_c = 6.0$ K), Tm ($T_c = 1.3$ K) are superconducting [15, 45]. At ambient pressure, the superconducting transition at $T_{c1} = 1.3$ K in $\text{Tm}_2\text{Fe}_3\text{Si}_5$ is not complete, when the sample re-enters the normal state at $T_{c2} = 1.1$ K [45].

Among other $M_2T_3Si_5$ compounds, only $Y_2\text{Re}_3Si_5$ was found to become superconducting above 1 K [46]. Most striking is the absence of superconductivity for $Y_2T_3Si_5$ and $\text{Lu}_2T_3Si_5$ in which iron is replaced by the isoelectronic metals ruthenium or osmium [35, 46]. All these compounds show metallic behaviour, with resistivity ratios up to 20 [45, 46]. A broad maximum in the resistivity of $Y_2\text{Os}_3Si_5$ around 100 K was interpreted as possibly indicating a strain-sensitive phase transition in this compound [46].

The effect of hydrostatic pressure on T_c is among the largest known, with $dT_c/dp = -7 \times 10^{-5}$ K bar⁻¹ for $\text{Lu}_2\text{Fe}_3Si_5$ and $\text{Sc}_2\text{Fe}_3Si_5$ and $dT_c/dp = +33 \times 10^{-5}$ K bar⁻¹ for $Y_2\text{Fe}_3Si_5$ [47]. $\text{Tm}_2\text{Fe}_3Si_5$ also has a large positive pressure coefficient of T_c . In fact T_{c1} and T_{c2} become clearly separated under hydrostatic pressure [48].

In pseudoternary solid solutions $(M_{1-x}M'_x)_2\text{Fe}_3Si_5$ between pairs of superconducting compounds with $(M, M') \equiv \text{Lu}, \text{Sc}$ or Y, T_c is rapidly depressed to below 1 K for x values of only 0.1. Results on the series with $M \equiv \text{Lu}$ and $M' \equiv \text{Tb} - \text{Tm}$ indicate that the depression of T_c depends primarily on the size difference between M and M' [46].

The compounds $M_2\text{Fe}_3Si_5$ with $M \equiv \text{Sc}, \text{Y}, \text{Lu}$ show a large linear term in the superconducting heat capacity and a reduced normalized jump in the specific heat at T_c [49]. This anomalous heat capacity and the dramatic alloying and pressure effect are not understood at present but may be caused by a topologically complex Fermi surface in which pockets of electrons remain in the normal state [49].

The compounds $M_2\text{Fe}_3Si_5$ with $M \equiv \text{Sm}, \text{Gd} - \text{Yb}$ exhibit antiferromagnetic ordering, as determined in susceptibility [50], specific heat [51] and neutron diffraction [52 - 54] measurements. Multiple magnetic transitions were observed for samarium [51], terbium and erbium [50 - 53].

Neutron diffraction on $\text{Tb}_2\text{Fe}_3Si_5$ [52], $\text{Er}_2\text{Fe}_3Si_5$ [53] and $\text{Tm}_2\text{Fe}_3Si_5$ [54] reveal antiferromagnetic ordering of the rare earth moments with no contribution from iron. The terbium and erbium compounds have magnetic structures commensurate with the lattice at low temperatures, but show incommensurate ordering at higher temperatures, with a sinusoidal modulation along the [001] direction of the antiferromagnetic structure. The moments

are directed parallel to the [001] direction for terbium, but order in (001) planes for erbium, with a non-collinear arrangement along the [110] set of directions. The thulium compound shows commensurate antiferromagnetic ordering, similar to the commensurate structure of $\text{Er}_2\text{Fe}_3\text{Si}_5$ [54]. Mössbauer measurements on the iron nucleus show that iron carries no moment [50, 55 - 57]. Below the Néel temperature, the conduction electron polarization at the iron site opposes an applied field [56, 57]. ^{155}Gd , ^{166}Er [57] and ^{161}Dy Mössbauer effect studies [56] were used to determine the rare earth moment in the magnetically ordered state and to construct an approximate model of the crystalline electric field effects in the heavy rare earth members of the $\text{M}_2\text{Fe}_3\text{Si}_5$ family [57]. The results are consistent with the direction of the easy axis determined in susceptibility measurements on directionally solidified polycrystalline samples [50] and the neutron diffraction work.

Magnetic ordering via the Ruderman–Kittel–Kasuya–Yoshida interaction is indicated, with deviations of the ordering temperatures from the De Gennes rule due to crystalline electric field effects [51, 57].

3.4. Orthorhombic $\text{U}_2\text{Co}_3\text{Si}_5$ -type compounds

The relationship between the $\text{Sc}_2\text{Fe}_3\text{Si}_5$ - and $\text{U}_2\text{Co}_3\text{Si}_5$ -type structures has been pointed out above. The arrangements of the [001] columns leads to a different coordination of the transition metal and of silicon. In $\text{M}_2\text{T}_3\text{Si}_5$ compounds of the $\text{U}_2\text{Co}_3\text{Si}_5$ type, two-thirds of the T atoms are surrounded by a deformed square pyramid of silicon atoms and each of the remaining T atoms is in the centre of a silicon tetrahedron [42]. The latter T atoms form chains along the [001] direction ($d_{\text{T-T}} = 2.8 \text{ \AA}$ in $\text{Dy}_2\text{Rh}_3\text{Si}_5$ [17]; powder data). The rare earth atoms form a distorted square net deriving from the BaAl_4 -type structure with distances of 3.9 - 4.2 Å within the layers and interlayer distances of 5.4 - 6.2 Å [17]. A monoclinic deformation variant of this structure type has recently been reported for compounds $\text{M}_2\text{Co}_3\text{Si}_5$ with $\text{M} \equiv \text{Sc, Y, Lu and Dy}$ [58], which are not superconducting above 1.2 K.

The only known superconductors with the $\text{U}_2\text{Co}_3\text{Si}_5$ -type structure are $\text{La}_2\text{Rh}_3\text{Si}_5$ ($T_c = 4.4 \text{ K}$) and $\text{Y}_2\text{Rh}_3\text{Si}_5$ ($T_c = 2.7 \text{ K}$) [17] (powder data). The two compounds containing lanthanum and yttrium show Pauli paramagnetism with susceptibilities of $39 \times 10^{-6} \text{ e.m.u. (g atom)}^{-1}$ and $50 \times 10^{-6} \text{ e.m.u. (g atom)}^{-1}$ respectively measured at 300 K [17]. Curie–Weiss behaviour with effective moments slightly larger than those of the trivalent free ion has been reported for compounds $\text{M}_2\text{Rh}_3\text{Si}_5$ with $\text{M} \equiv \text{Nd, Gd, Tb, Dy, Ho and Er}$ [17]. $\text{Tb}_2\text{Rh}_3\text{Si}_5$ has a Néel temperature of 8.5 K [17].

3.5. Body-centred tetragonal LaPtSi -type and primitive cubic LaIrSi -type compounds

Of the known ternary equiatomic structure classes (for a review see refs. 11 and 59), only three have members that were reported to be superconducting; the hexagonal Fe_2P -type derivatives [4] (see also ref. 32), the tetragonal ThSi_2 derivative LaPtSi -type structure [19, 20, 60] and the cubic SrSi_2 derivative LaIrSi -type structure [61, 62]. In both the latter structures,

each silicon has three T and each T has three close silicon neighbours, ($d_{\text{Si-Ir}} = 2.315 \text{ \AA}$ [61]; $d_{\text{Si-Pt}} = 2.41 - 2.45 \text{ \AA}$ [20]). The Si-T framework is three dimensional, while the spatial arrangement is different in both structures (Fig. 4).

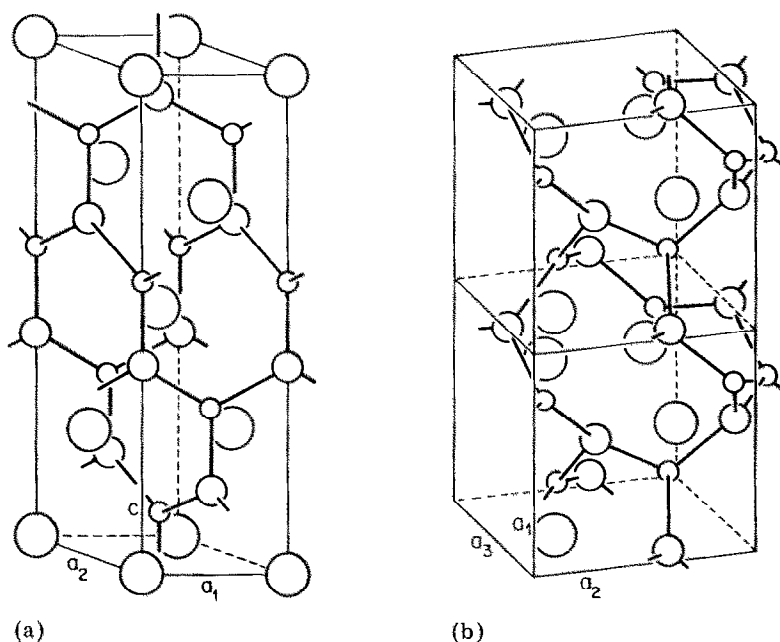


Fig. 4. The structures of (a) tetragonal LaPtSi and (b) cubic LaIrSi: \bigcirc , lanthanum; \bigcirc , platinum or iridium; \circ , silicon. (After Parthé and Chabot [11].)

The known superconducting compounds with the tetragonal LaPtSi-type structure are listed in Table 2. Evers *et al.* [60] found a superconducting onset at 4.5 K in tetragonal LaIrGe, but ascribed it to an impurity phase.

TABLE 2
Superconducting compounds with the tetragonal LaPtSi-type structure

| Compound | T_c (K) | a (\AA) | c (\AA) | Reference |
|--|-----------|----------------------|----------------------|-----------|
| LaPtSi | 3.48 | 4.249(3) | 14.54(1) | [19] |
| | 3.3 | 4.245(5) | 14.54(3) | [60] |
| LaIrGe | 1.64 | 4.317(3) | 14.41(1) | [63] |
| LaPtGe | 3.53 | 4.266(2) | 14.95(1) | [19] |
| | 3.4 | 4.266(5) | 14.96(3) | [60] |
| ThIrSi ^a | 6.50 | 4.143 ^b | 14.28 ^b | [64] |
| ThRh _{0.96} Si _{1.04} ^a | 6.45 | 4.130 ^b | 14.28 ^b | [64] |

^a Powder data (atomic ordering not established [64]).

^b Taken from ref. 64, Fig. 3.

Isotypic [20] MPtSi compounds with neodymium ($T_m = 15$ K) and samarium ($T_m = 4$ K) show magnetic ordering, those with cerium and praseodymium remain paramagnetic down to 2 K [37]. CePtSi does not show superconductivity above 70 mK [65].

In ThSi₂-type solid solutions Th(Si_{1-x}T_x)₂, with T ≡ Ir and Rh, T_c falls from 3.2 K at $x = 0$ to below 1.7 at $x \approx 0.25$, but reappears at $x > 0.7$ and reaches maximum values (Table 2) for $x \approx 1$ [64]. It was inferred from powder data that iridium and silicon are distributed at random over the available sites in ThIrSi [64]. The difficulties in assessing atomic ordering from powder data in this structure class were discussed by Klepp and Parthé [20]. The T_c variation at $x > 0.7$ is rather suggestive of an atomic ordering phenomenon, however, and it may thus be justified to classify these phases among the LaPtSi-type compounds.

Chevalier *et al.* [62] report the superconductivity of cubic LaRhSi and LaIrSi in arc-melted samples, annealed at 800 °C for 4 days. Unpublished work by the present author [23] on arc-melted samples annealed at 900 or 1000 °C for 6 days does not indicate superconductivity above 1 K in LaRhSi, and superconductivity below 2 K in LaIrSi was identified as being due to impurity phases, consistent with the results by Evers *et al.* [60] on their cubic LaIrSi. The variation in lattice parameters (Table 3) possibly indicates a homogeneity range for the compounds, allowing the interpretation that T_c of the LaTSi phases might vary with composition. However, this explanation does not appear to hold for LaRhSi (see Section 4). Cubic NdIrSi is reported to show spontaneous magnetization below 10 K [62].

TABLE 3

Cubic LaIrSi-type phases

| Compound | T_c (K) | Annealing conditions | a (Å) | Reference |
|----------|----------------|----------------------|----------|-----------|
| LaRhSi | 4.35 | 800 °C for 4 days | 6.296(2) | [62] |
| LaRhSi | — ^a | 900 °C for 6 days | 6.356(2) | [23, 63] |
| LaIrSi | 2.3 | 800 °C for 4 days | 6.337(2) | [62] |
| LaIrSi | — ^b | 1000 °C for 6 days | 6.371(2) | [23, 63] |

^a Not superconducting above 1.2 K.

^b 1.9 - 1.6 K because of impurities of LaIr₂Si₂ (high temperature) and La₃Ir_{≈1}Si_{≈1}.

3.6. CeNiSi₂-type compounds

The CeNiSi₂-type structure [22] is made up of slabs of silicon-centred trigonal rare earth prisms, alternating with slabs of fused (distorted) square antiprisms Si₄R₄ centred by cobalt (Fig. 5). Transition metal and silicon atoms form a three-dimensional network. Each T atom has five near silicon neighbours ($d_{T-Si} = 2.37 - 2.43$ Å), and the silicon atoms form zigzag chains along the [001] direction ($d_{Si-Si} = 2.55$ Å) and planar layers with a rather long Si-Si distance (3.0 Å). (All distances are calculated for LaRhSi₂ [63].)

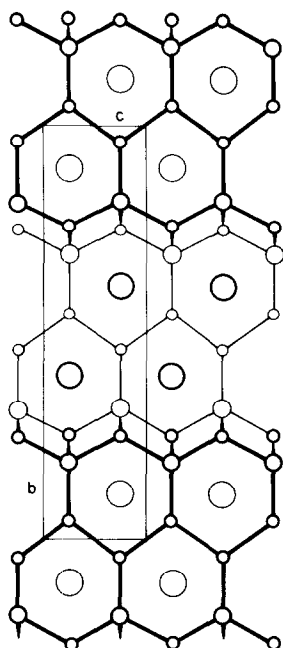


Fig. 5. Projection of the CeNiSi_2 -type structure along the $[100]$ direction. The Ni-Si net is outlined: —, $x = 0$; - - -, $x = \pm 1/2$.

A complete list of isotypic compounds and a discussion of related structure types are given in ref. 11.

Information on superconducting compounds with this structure is sparse (Table 4). An onset to superconductivity was seen in YCoSi_2 at 1.2 K [66]; however, it was not established whether this is due to the CeNiSi_2 -type phase or to some impurity. MCoSi_2 compounds with $M \equiv \text{Y}$, Ce show temperature-independent Pauli paramagnetism [66], while compounds with $M \equiv \text{Nd}$, Sm, Gd, Tb, Ho, Er and Tm show antiferromagnetic ordering below 20 K [66]. The effective rare earth moments in the paramagnetic state agree well with the free-ion values, and, for Tb-Tm, the Néel temperatures vary

TABLE 4

Superconducting compounds with the orthorhombic CeNiSi_2 -type structure

| Compound | T_c (K) | a (Å) | b (Å) | c (Å) | Reference |
|-------------------|------------------|----------------|-----------|----------|-----------|
| LaRhSi_2 | 3.42 | — ^a | — | — | [21] |
| LaRhSi_2 | 3.26 | 4.324(2) | 16.84(1) | 4.202(2) | [23] |
| LaIrSi_2 | 2.03 | — ^a | — | — | [21] |
| LaIrSi_2 | 2.30 | 4.323(3) | 16.84(1) | 4.227(4) | [23] |
| YCoSi_2 | 1.2 ^b | 4.025(2) | 16.280(7) | 3.963(3) | [66] |

^a No lattice parameters given.

^b Superconductivity of the CeNiSi_2 -type phase not unequivocally established.

with the De Gennes factor [66]. There is no evidence for a magnetic contribution from the cobalt sublattice [66]. In the MTSi_2 series with $T \equiv \text{Ir}$ or Rh , the CeNiSi_2 type is obtained with $M \equiv \text{La}$, Ce , Nd , Sm in annealed (950°C for 4 days) and with gadolinium in quenched samples [21]. The appearance of spontaneous magnetization is reported for the neodymium compounds at low temperature and antiferromagnetism for the gadolinium compound [21].

3.7. BaNiSn_3 -type compounds

The BaNiSn_3 -type compound [25] is a BaAl_4 derivative structure [44] (Fig. 3) and will be discussed with CaBe_2Ge_2 -type and ThCr_2Si_2 -type compounds in Section 3.8.

Crystallographic and superconductivity data of all known isotypic silicides are listed in Table 5. Lejay *et al.* [24] report superconductivity of LaRhSi_3 and LaIrSi_3 between 2.7 and 1.9 K, determined by resistivity measurements, and find variations with composition and heat treatment of their specimens. The other results reported in Table 5 were obtained by a.c. susceptibility measurements on annealed specimens (950°C for 6 days), prepared with a slight nominal excess of silicon (2 - 4 at.%) to avoid the formation of CeNiSi_2 -type impurities [44].

TABLE 5

Compounds with the tetragonal BaNiSn_3 -type structure

| Compound | T_c (K) | a (Å) | c (Å) | Reference |
|-------------------|----------------|--------------------|-------------------|-----------|
| LaCoSi_3 | — ^a | 4.1868(8) | 9.654(2) | [11] |
| CeCoSi_3 | — ^a | 4.1344(8) | 9.561(3) | [11] |
| LaRhSi_3 | 2.7 - 2.2 | 4.272 ^b | 9.83 ^b | [24] |
| LaRhSi_3 | 2.3 | 4.268(1) | 9.829(3) | [23] |
| LaIrSi_3 | — ^c | 4.278(5) | 9.83(1) | [24] |
| LaIrSi_3 | — ^d | 4.282(1) | 9.838(3) | [23, 44] |

^a Not determined.

^b No errors given.

^c T_c between 2.7 and 1.9 K (not specified).

^d Not superconducting above 1.2 K.

3.8. Compounds with CaBe_2Ge_2 - and ThCr_2Si_2 -type structures

The structure types CaBe_2Ge_2 [27], ThCr_2Si_2 [29] and BaNiSn_3 [25] are ordered ternary derivatives of the binary BaAl_4 -type structure [67], shown in Fig. 6. The aluminium atoms occupy two types of sites, with tetrahedral coordination by four aluminium atoms (and four barium atoms) and with pyramidal coordination by five aluminium atoms (and five barium atoms). The tetrahedral (t) and pyramidal (p) sites are arranged in layers perpendicular to the [001] direction in the sequence ptp ptp. Planes of barium atoms are intercalated between ptp groups of aluminium layers. As

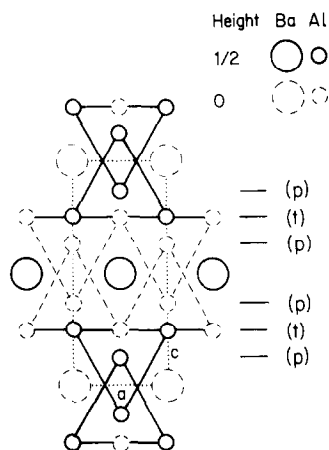


Fig. 6. Structure of BaAl_4 projected along the $[100]$ direction: p, pyramidal sites; t, tetrahedral aluminium sites. The contours outline the pyramids. (After Engel *et al.* [44].)

pointed out above, the pyramidal sites are usually termed antiprismatic sites, since the bases of the aluminium and barium pyramids form a distorted square antiprism. In the three ternary derivative structures, the aluminium sites are occupied by transition metal (T) and silicon, or homologue, (X) atoms in an ordered fashion, forming three-dimensional T-X networks. The three structures are distinguished by the different distribution of T and X atoms over the p and t layers (Fig. 3): XTX XTX in ThCr_2Si_2 , TXT XTX in CaBe_2Ge_2 and TXX TXX in BaNiSn_3 [26, 44]. Other hypothetical ordering variants are discussed in ref. 42.

All three structure types are observed in the system La-Ir-Si [44]. Relevant interatomic distances may be taken from Fig. 3. The heteronuclear Ir-Si distances are short ($2.40 \pm 0.04 \text{ \AA}$) and correspond to the sum of the covalent radii (coordination number 12 radii for the metal atoms), all other interatomic distances, in particular the homonuclear Si-Si distance (2.61 \AA), are longer than the sums of their covalent radii [44]. The intralayer distances of the lanthanum atoms are equal to the crystallographic a axis dimension ($4.1 - 4.3 \text{ \AA}$), the interlayer La-La distances are larger ($5.7 - 5.9 \text{ \AA}$).

The CaBe_2Ge_2 -type and ThCr_2Si_2 -type structures are observed as high and low temperature modifications of LaIr_2Si_2 [26] (single-crystal refinement). The transformation temperature varies with composition and drops from about $1720 \text{ }^\circ\text{C}$ for nominally stoichiometric (possibly iridium rich) samples to below $1000 \text{ }^\circ\text{C}$ for silicon-rich samples [26]. The high temperature form may be stabilized to room temperature by quenching, and is superconducting at 1.6 K , while the low temperature form is normal down to 1 K [26]. Specific heat measurements on both modifications reveal bulk superconductivity in the high temperature phase, an electronic specific heat coefficient γ of $1.7 \text{ mJ K}^{-2} (\text{g atom})^{-1}$ and $0.9 \text{ mJ K}^{-2} (\text{g atom})^{-1}$ and Debye temperatures $\theta_D(0)$ of 300 K and 385 K for the high and low temper-

ature phases respectively [68]. Band structure calculations for both phases are in good agreement with the experimental results and indicate strong Ir–Si hybridization effects in the high temperature phase with mainly d character at E_F [68].

Lejay *et al.* [69] find similar polymorphism in YIr_2Si_2 . Resistivity measurements show transitions into the superconducting state with an onset at 2.8 K for both phases; however, the transition for the low temperature phase ($ThCr_2Si_2$ type) is not complete at 2.0 K [69].

Superconductivity was reported for $ThCr_2Si_2$ -type $LaRh_2Si_2$ ($T_c = 3.8$ K [70], $T_c = 3.9$ K [21]) and YRh_2Si_2 ($T_c = 3.1$ K [21, 70]), with Pauli paramagnetism [21] or “itinerant electron magnetic ordering” [70] above the superconducting transition temperature. The resistive transition in $LaRh_2Si_2$ is rather broad (4.1 - 2.5 K) [70] and accompanied by no jump, but by a “change in slope at 3.8 K” in the specific heat [70]. Neutron diffraction reveals antiferromagnetic ordering of the rare earth sublattice with moments parallel to the [001] direction in $TbRh_2Si_2$ ($T_N = 92$ K; type I antiferromagnet) and $CeRh_2Si_2$ ($T_N = 36$ K, type II antiferromagnet), with no evidence of any moment on the rhodium atoms [71].

In a survey of 27 compounds MT_2X_2 with $M \equiv Y, La, Th, U, T \equiv Ru, Rh, Pd, Os, Ir, Pt$ and $X \equiv Si$ or Ge [72], superconductivity above 1.1 K was found only in phases with the $CaBe_2Ge_2$ -type structure, but never in phases with the $ThCr_2Si_2$ -type structure. The case of $LaRh_2Si_2$ is discussed in Section 4.

Superconductivity below 1.2 K was found in the germanides $YbPd_2Ge_2$, $LaPd_2Ge_2$ and $LaNi_2Ge_2$ with the $ThCr_2Si_2$ -type structure, and in $LaPt_2Ge_2$ whose structure was given as $BaAl_4$ related [73, 74].

An unusual compound is $CeCu_2Si_2$ ($ThCr_2Si_2$ type) which shows at $T_c = 0.6$ K a transition from a “Fermi liquid” state into a superconducting state, which is carried by pairs of heavy fermions [28]. The transition temperature varies rapidly with composition of the $CeCu_2Si_2$ phase, falling from 0.67 K for copper-rich samples to below 40 mK for copper-poor samples, with a variation of about 2 at.% in the copper concentration [75, 76]. The phase forms peritectically at 1540 °C, and there is no evidence for a high temperature polymorphic transformation [75, 77]. Vacancy concentrations on copper sites up to 20% were reported [78] but not confirmed in later work [79, 80]. For a review of the properties of $CeCu_2Si_2$, we refer to Spille *et al.* [76]. More recent work includes specific heat [77, 81] and transport measurements [77, 82] on non-superconducting and superconducting single crystals, band structure calculations for $CeCu_2Si_2$ and $LaCu_2Si_2$ [80] and theories of superconductivity in the heavy fermion system $CeCu_2Si_2$ [83, 84].

The $ThCr_2Si_2$ structure forms with a large number of elements and is, in fact, the most frequent structure type found in rare earth–transition metal boride, silicide and germanide systems [11]. This structure proves to be ideal for the study of rare earth systems with an ordered rare earth lattice as evidenced by a vast body of literature on intermediate valence and on

neutron diffraction studies of magnetic ordering in ThCr_2Si_2 -type compounds. Any attempt at listing this literature would lead far beyond the scope of the present review.

4. Non-superconducting phases

Our picture of the phenomenon of superconductivity in ternary compounds will remain incomplete if the non-superconducting phases are overlooked. Since the number of such phases is considerable, the present survey will forego a discussion of their structures and will be strictly limited to those ternary systems that contain a superconducting phase and for which at least part of an isothermal section has been established. This is the case for Sc-Fe-Si [85] (800 °C: 14 ternary phases, one known superconductor), Sc-Co-Si [86] (67 at.% Sc or less, 800 °C: 12 ternary phases, one superconductor), Sc-Rh-Si [5] (40 at.% Si or more, 1000 °C: nine ternary phases, two superconductors), Y-Fe-Si [87] (800 °C: seven ternary phases, one superconductor), Y-Co-Si [88] (33 at.% Y or less, 800 °C; 33 at.% Y or more, 600 °C: five ternary phases, one superconductor (?)), Y-Re-Si [89] (800 °C: two ternary phases, one superconductor) and Ce-Cu-Si [90] (33 at.% Ce or less, 600 °C: five ternary phases, one superconductor). Some of the equilibria at 950 °C in La-Rh-Si (but *cf.* ref. 24 (900 °C)) were reported by Chevalier *et al.* [21]. A more extended portion of an isothermal section (60 at.% La or less, 900 °C: eight identified ternary phases, four superconductors) [63], based on powder X-ray diffraction and metallographic analysis, is presented in Fig. 7. Most of the structure types encountered in these ternary systems are discussed in ref. 11.

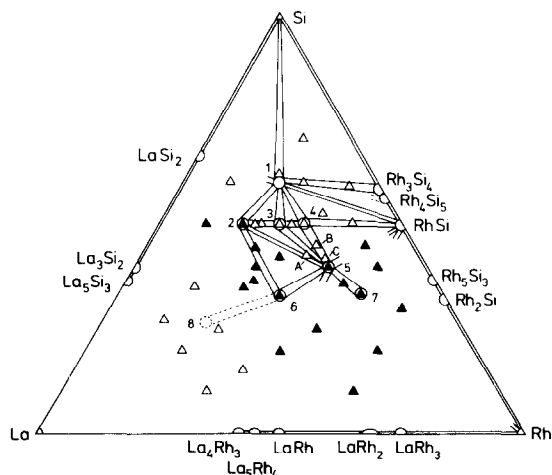


Fig. 7. Some phase equilibria at 900 °C in the system La-Rh-Si: ○, composition of phases (1, LaRhSi_3 ; 2, $\text{La}_2\text{Rh}_3\text{Si}_3$; 3, LaRhSi_2 ; 4, $\text{La}_2\text{Rh}_3\text{Si}_5$; 5, LaRh_2Si_2 ; 6, LaRhSi ; 7, LaRh_3Si_2 ; 8, $\text{La}_3\text{Rh}_{\approx 1}\text{Si}_{\approx 1}$); Δ, superconducting samples; ▲, non-superconducting samples; A, B, C, discussed in the text.

A sample of stoichiometric composition LaRhSi was not superconducting above 1.2 K. The existence of a composition-dependent superconductivity of this phase appears to be ruled out, since samples prepared at various compositions around the equiatomic composition did not superconduct (Fig. 7). Instead, superconductivity at 4.4 K was found in more lanthanum-rich samples, and ascribed to phase 8 (Fig. 7), of composition $\text{La}_3\text{Rh}_{\approx 1}\text{Si}_{\approx 1}$.

Similarly, LaRh_2Si_2 was not superconducting above 1.2 K while non-stoichiometric samples (Fig. 7, A, B and C) had superconducting onset temperatures of 3.4 K (A) and 4.1 K (B, C), determined by χ_{ac} susceptibility (20 Hz) measurements. The same samples showed a reduced amplitude of the superconducting signals after powdering (60% in A and B; 30% in C), consistent with the superconductivity of A being due to its content in LaRhSi_2 (Fig. 7, phase 3) and that of B and C due to their content in $\text{La}_2\text{Rh}_3\text{Si}_5$ (Fig. 7, phase 4).

5. Trends

Observation of systematic trends associated with superconductivity may provide guidelines for future research. The valence electron concentration (VEC) rules proposed by Matthias [91] have been most successful for optimizing T_c in certain classes of binary compounds. Conventionally calculated VECs are not an accurate tool, however, in predicting high T_c values for ternary compounds [92]. Another aspect of unusual superconductors is that of transition metal clustering, first pointed out by Vandenberg and Matthias [93]. Physically important clustering has been found to be correlated with the occurrence of significant charge transfer to or from the clusters within the structure, influencing the superconducting and other properties, as demonstrated convincingly for the Chevrel phases by Yvon [94] and others [8] using concepts of bonding. Similar considerations are not easily applied to other ternary compounds, since their bonding cannot be rationalized in a simple way and, in particular, since the formal oxidation states of the non-metals, *e.g.* silicon, cannot be derived unambiguously from simple interpretation of interatomic distances [92]. Bond models have been applied to the silicides containing iron or cobalt to explain the loss of magnetic moment [35, 95].

Three-dimensional transition metal clusters such as the Mo_6 octahedra or Rh_4 tetrahedra, well separated from the rest of the structure, are not present in the silicides. The structure class ($\text{Sc}_5\text{Co}_4\text{Si}_{10}$) with the highest T_c representative has no T-T contacts. Transition metal clustering is limited to two-dimensional triangles (LaRu_3Si_2), squares ($\text{Sc}_2\text{Fe}_3\text{Si}_5$) or one-dimensional chains ($\text{Sc}_2\text{Fe}_3\text{Si}_5$, $\text{U}_2\text{Co}_3\text{Si}_5$). A feature common to all these silicide structures is the occurrence of short T-Si contacts, indicative of covalent interactions. Most of the compounds of Section 3 are characterized by the existence of a three-dimensional T-Si skeleton. The distribution of the T and silicon atoms and the topology of their network have a strong influence on

the superconducting properties, illustrated in the closely related pairs LaPtSi and LaIrSi and high and low temperature LaIr₂Si₂ with CaBe₂Ge₂- and ThCr₂Si₂-type structures. Most striking is the appearance of superconductivity in a number of compounds containing infinite slabs taken from the CaBe₂Ge₂ structure type (Sc₂Fe₃Si₅; La₂Rh₃Si₅ with U₂Co₃Si₅ type; LaIr₂Si₂ (high temperature) with CaBe₂Ge₂ type). In this latter structure type, the T and silicon atoms alternate on adjacent sites of a three-dimensional network, and each T has five silicon nearest neighbours. Very similar features are found in the structure type of Sc₅Co₄Si₁₀.

A more quantitative interpretation will become possible with the availability of band structure calculations. Such calculations, carried out for binary silicides of near-noble metals reveal important d-p hybridization, with silicon s electrons not participating. The situation in the disilicides of nickel and cobalt is different. The silicon sp³ hybrid is nearly unchanged and the density of states on silicon, which is free electron like, is the predominant contribution at E_F [96]. The large unit cells of superconducting ternary silicides make band structure calculations a rather time-consuming undertaking. So far, results have been obtained for two structure types, ThCr₂Si₂ and CaBe₂Ge₂. A comparison of band structures for the two LaIr₂Si₂ modifications reveals that the CaBe₂Ge₂-type arrangement leads to an increased density of states at E_F with predominant d character and a non-negligible silicon p contribution. It remains to be seen whether this can be generalized to compounds with similar structural features.

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