Structure and superconductivity studies on ternary equiatomic silicides, MM'Si[†]

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Abstract. A series of ternary equiatomic transition metal silicides MM'Si (M = Zr, Nb, Ta; M' = Ru, Re) and $Zr_{1/2}M_{1/2}$ RuSi (M = Nb, Ta) have been synthesized and characterized. Guinier x-ray data clearly indicate that the compounds MM'Si (M = Nb, Ta; M' = Ru, Re) crystallize with the orthorhombic TiFeSi-structure. This is contrary to one of the literature reports ascribing the hexagonal ZrRuSi structure to MReSi, M = Nb, Ta. ZrRuSi and $Zr_{1/2}M_{1/2}$RuSi (M = Nb, Ta), however, crystallize with the ZrRuSi structure. All the compounds are metallic and exhibit small and negative Seebeck coefficients. Superconductivity has been discovered in MM'Si, M = Nb, Ta; M' = Ru, Re and the transition temperatures, as measured by the low frequency a.c. susceptibility technique, range from 2·7 to 5·1 K. $Zr_{1/2}Nb_{1/2}$RuSi is not superconducting above 2·2 K. The observed properties are explained in terms of the electronic charge transfer effects and crystal structures adopted by these metal excess ternary silicides.

Keywords. Metal excess systems; silicides; superconducting compounds; ternary systems.

1. Introduction

A large number of equiatomic ternary metal excess compounds of the type $MM'X$ where M and M' represent transition metals and X is a non-metal (X = Si, Ge, B, P, As or metal—Al, Ga, In, Sn) are known (Rundqvist and Nawapong 1966; Jeitschko 1968; Johnson and Jeitschko 1972; Dwight 1974; Barz et al 1980; Johnston and Braun 1982; Meisner et al 1983; Muller et al 1983; Patil et al 1983). In addition, a large number of compounds with M = rare earth or Y are also known (Hovestreydt et al 1982; Klepp and Parthé 1982; Chevalier et al 1982a, b; Mazzone et al 1983; Rossi et al 1983; Braun 1984; Kido et al 1984; Parthé and Chabot 1984). These compounds basically crystallize in any one of the following structure types: (i) Hexagonal (ZrNiAl or Fe₂P-type; space group $P\bar{6}2m$; Z = 3), (ii) Orthorhombic (TiNiSi or Co₂P or anti-PbCl₂ type; $Pnma$; Z = 4), (iii) Orthorhombic (CeCu₂-type; $Imma$; Z = 4), (iv) Hexagonal (MgZn₂-type; $P6_3/mmc$; Z = 4), (v) Hexagonal (Ni₂In-type; $P6_3/mmc$; Z = 2), (vi) Tetragonal (PbCl-type; $P4/nmm$; Z = 2). In addition, some phases exhibit an orthorhombic

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† Dedicated to the memory of Prof. N S Satya Murthy.

(TiFeSi-type; space group $Ima2$; $Z = 12$) structure which is a deformed ZrNiAl-type structure. The synthesis and crystallography of many of the 1:1:1 phases are reported in literature over the years. A survey of the structure types of the presently known equiatomic (1:1:1) ternary transition metal (or rare earth including Y and Sc) silicides and germanides are presented in tables 1 and 2 whereas those of the phosphides, arsenides and borides are given in table 3.

Only a few of the known ternary 1:1:1 compounds have been examined for the exhibition of superconductivity so far in the literature and they belong to the following four structure types: (i) Phosphides and arsenides with the Fe_2P (hexagonal ZrNiAl) and Co_2P (orthorhombic TiNiSi) structure, (ii) Silicides and germanides with the tetragonal LaPtSi and cubic LaIrSi structure. The available T_c data for the above two systems are listed in table 4. High temperature superconductivity with a T_c of 13 K has been discovered in ZrRuP with the Fe_2P structure (table 4) (Barz $et\ al$ 1980; Meisner and Ku 1981). Analogues of the ZrRuP (e.g., HfRuP; ZrRuAs with the Fe_2P structure) also exhibit high T_c. On the other hand, another polymorph of ZrRuP and its

Table 1. Survey of the structure types of the equiatomic ternary transition metal silicides and germanides (after Johnson and Jeitschko 1972, with some modification)

Table 2. Survey of the structure types of the equiatomic ternary rare earth (including yttrium and scandium) silicides and germanides with transition metals of the iron, cobalt and nickel groups (after Hovestreydt *et al* 1982)

Silicides

	Fe	Co	Ni
La	◊	◊	
Ce	◊	◊	▣
Pr	◊	◊	▣
Nd	◊	◊	▣
Sm	◊	◊	
Eu			
Gd	◊	◊	□
Tb	◊		□
Dy	◊		□
Ho	◊		□
Er			□
Tm			
Yb	◊		
Lu			□
Y	◊		□
Sc		□	□

	Ru	Rh	Pd
La		○	
Ce			
Pr			
Nd			
Sm			
Eu			
Gd		□	
Tb		□	
Dy		□	
Ho		□	
Er		□	
Tm			
Yb			
Lu			
Y		□	
Sc	△	□	□

	Os	Ir	Pt
La		○	▣
Ce			▣
Pr			▣
Nd		○	▣
Sm			▣
Eu			
Gd		□	▣
Tb			□
Dy			□
Ho			□
Er		□	□
Tm			□
Yb			
Lu			□
Y		□	□
Sc		□	□

Germanides

	Fe	Co	Ni
La			
Ce			
Pr			
Nd			
Sm			
Eu			
Gd		□	□
Tb			□
Dy			
Ho		□	□
Er			□
Tm			
Yb			
Lu		□	□
Y		·	□
Sc		□	□

	Ru	Rh	Pd
La			⊞
Ce		□	⊞
Pr		□	⊞
Nd		□	⊞
Sm		□	⊞
Eu			
Gd		□	⊞
Tb		□	⊞
Dy		□	⊞
Ho		□	⊞
Er		□	⊞
Tm		□	⊞
Yb			
Lu			
Y		□	⊞
Sc	△	□ △	△

	Os	Ir	Pt
La		▣	▣
Ce		□	▣
Pr		□	▣
Nd		□	▣
Sm		□	□
Eu			
Gd		□	□
Tb		□	□
Dy		□	□
Ho		□	□
Er		□	□
Tm		□	□
Yb			
Lu			
Y		□	□
Sc	△	□	□

◊ PbFCl (tetragonal) ⊞ CeCu$_2$ (orthorhombic)
△ ZrNiAl (hexagonal) ▣ LaPtSi (tetragonal)
□ TiNiSi (orthorhombic) ○ LaIrSi (cubic)

Rare earth - transition metal gallides LnM'Ga (M'= Ni, Pd, Pt, Rh and Ir) adopt the TiNiSi structure with the single exception of CeNiSi which adopts the ZrNiAl structure (Hovestreydt et al 1982)

representatives (e.g., NbRuP, TaRhP, etc.; table 4) crystallizing with the Co_2P (TiNiSi-type) structure possess low T_c (< 4.5 K) (Muller *et al* 1983). Thus, crystal structure plays an important role in giving rise to high T_c. This is corroborated by the heat capacity studies on ZrRuP carried out by Stewart *et al* (1982) which showed large electron-

Table 3. Survey of the structure types of the equiatomic ternary transition metal phosphides, arsenides and borides (after Fruchart 1982; Rundqvist and Nawapong 1966; Jeitschko 1968, with some modification)

Phosphides

	Fe	Co	Ni
Ti	□	□	
Zr	□	□	▲
Hf			
V	□	□	□
Nb	□	□	□
Ta	□	□	□
Mo	□	□	△
W		□	△
Mn	□	□	

Arsenides

	Fe	Co	Ni
Ti	△		
V	△	□	□
Nb	□	□	□
Ta	□	□	□
Mn	X	□	△

Borides

	Fe	Co	Ni
Ta	△		■
Mo	△		■
W		□	
Mn	□	□	

	Ru	Rh	Pd
Ti	△		
Zr	△□	□	
Hf	△		
V	□	□	
Nb	□	□	
Ta	□	□	

	Ru	Rh	Pd
Ti		□	△
Zr	△		
Hf	△ △		
V		□	

△ ZrNiAl (hexagonal)
□ TiNiSi (orthorhombic)
△ TiFeSi (orthorhombic)

X Fe$_2$As (tetragonal)
▲ Ni$_2$In (hexagonal)
■ MoAlB (orthorhombic)

phonon interaction and relatively low values of the $N(0)$, the density of states at the Fermi level.

It is interesting to note that ZrRuSi, crystallizing with the Fe$_2$P structure similar to ZrRuP, does not exhibit superconductivity above 1·2 K, the limit of temperature measurement even though the compound is metallic (Johnston and Braun 1982; Barz et al 1980). This proves that charge transfer effects and the non-metallic constituent (X = Si or P) play an important role in inducing superconductivity. Since P or Si atoms are isolated in the structure (no P-P or Si-Si bonds exist) it is reasonable to assume that they are present as P^{3-} and Si^{4-} in ZrRuP and ZrRuSi respectively. Since zirconium is always tetravalent there is no effective charge transfer from Zr to Ru in Zr^{4+} RuSi^{4-} whereas one electron is contributed to Ru conduction band in Zr^{4+} RuP^{3-}. Similar considerations can be applied to the isostructural series of compounds NbRuSi, NbRhP, ScRuSi, etc. where changes in electronic band structure are effected by changes in X and M atoms and where the M' transition metal atoms act as a source or sink of electrons.

Table 4. T_c data on equiatomic $MM'X$ ternary phases (taken from Subba Rao and Geetha Balakrishnan 1984; Braun 1984)

I. Phosphides and arsenides (X = P, As)

Hexagonal structure (Fe_2P-type)				Orthorhombic structure (Co_2P-type)	
Phase	T_c, K	Phase	T_c, K	Phase	T_c, K
TiRuP	1·3	—	—	ZrRuP	3·46
ZrRuP	13·0	ZrRuAs	11·7	ZrRhP	< 1·1
HfRuP	10·9	HfRuAs	4·9	NbRuP	—
TiOsP	1·2	—	—	NbRhP	4·08
ZrOsP	7·4	ZrOsAs	8·0	TaRuP	—
HfOsP	6·1	HfOsAs	3·2	TaRhP	4·41

II. Silicides and germanides (X = Si, Ge)
Tetragonal LaPtSi type structure

Compound	T_c, K
LaPtSi	3·48
LaIrGe	1·64
LaPtGe	3·53
ThIrSi	6·50
$ThRh_{0·96}Si_{1·04}$	6·45

Superconductivity has been established in precious-metal containing tetragonal $ThSi_2$ derivatives of the LaPtSi-type (table 4) (Braun 1984). The T_c values range from 1·6 to 6·5 K. Reports on the superconductivity of the cubic $SrSi_2$-derivatives of the LaIrSi structure types (e.g., LaRhSi, LaIrSi) have not been confirmed by other investigators (Chevalier *et al* 1982a; Braun 1984; Evers *et al* 1984). Detailed studies are yet to be made.

2. Structural aspects

Since a very large number of $MM'X$ phases crystallize in the ZrNiAl, TiNiSi or their derivative structures a brief account of the structural aspects is in order and is given below.

2.1 *The ZrRuSi structure*

ZrRuSi crystallizes in the hexagonal ordered Fe_2P-type structure, Zr and Ru atoms occupying crystallographically inequivalent sites of the binary structure. The lattice parameters are: $a = 6·68$ Å; $c = 3·67$ Å (Johnson and Jeitschko 1972). The structure contains a nearly rhombohedral $MM'X$ subcell as a fundamental building block. Figure 1a gives the structure of ZrRuSi and figure 1b gives the projection along the hexagonal c-axis. The M'(Ru) and M(Zr) crystallographic sites are coordinated by a tetrahedron and tetragonal pyramid respectively of silicon atoms. The MM' inter-
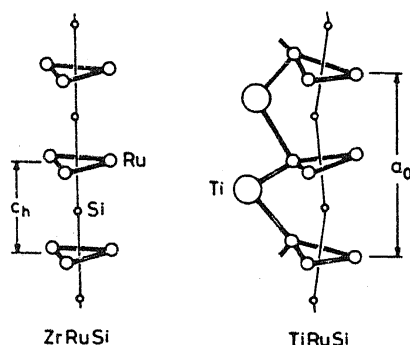
O Ru   o Si   z = 0

◯ Zr   ● Si   z = 1/2

(a)   (b)

Figure 1. (a) Structure of ZrRuSi. The subcell is indicated by the heavy lines and the hexagonal unit cell is shown at the top. (b) Projection of the ZrRuSi structure along the hexagonal c-axis. Thick lines represent the metallic bonding of the Zr-Ru chains and Ru-Ru triangular clusters. The dashed line indicates the boundary of the hexagonal unit cell.

atomic distances are short (Zr-Ru distance ~ 3 Å). The rhombohedral subcells are stacked to form columns parallel to the c-axis of the hexagonal unit cell and contain $M'M$ zigzag chains. The columns are grouped together permitting the formation of triangular clusters of M'(Ru) atoms (figure 1). This leads to a layer type structure with each layer occupied by either M(Zr) and X(Si) or M'(Ru) and X(Si) atoms, and separated by a distance of $c/2$. The two dimensional planar framework of M(Zr) and M'(Ru) atoms is therefore an important feature of this structure.

2.2 *The TiFeSi structure*

The TiFeSi structure is a superstructure modification of the ZrRuSi type phase (Jeitschko 1970a, b). It arises from small displacements (upto ~ 0.4 Å) of the atoms from their ideal hexagonal positions causing a reduction in symmetry from hexagonal to body centered orthorhombic. The interatomic distances are, however, not much affected by these shifts since the positions of the neighbouring atoms are adjusted accordingly. The lattice constants of the TiFeSi structure are related to the hexagonal lattice parameters by $a_{\text{ortho}} \approx 2c_{\text{hexa}}$, $b_{\text{ortho}} \approx \sqrt{3}\, a_{\text{hexa}}$ and $c_{\text{ortho}} \approx a_{\text{hexa}}$. These displacements cause a transverse bending distortion of the Ru trigonal prisms (figure 2). The tilt of the Ru triangles alternates along the column axis, causing a doubling of the lattice parameter and a reduction of the symmetry from hexagonal to orthorhombic. The TiFeSi superstructure has been observed (table 1) for TiFeSi, TiRuSi, TiFeGe, ZrRuGe, NbFeGe, Ti(Co$_{1-x}$Fe$_x$)Ge for $x > 0.1$, and HfRuAs (low temperature phase) (Johnson and Jeitschko 1972; Jeitschko 1970a, b; Jeitschko and Johnson 1975; Meisner 1983).

Figure 2. The distortion of the stacked trigonal prisms in ZrRuSi leading to the TiFeSi-type superstructure. The tilt of the Ru triangles alternates along the column axis causing a doubling of the lattice parameter and a reduction of the symmetry from hexagonal to orthorhombic.

2.3 *The TiNiSi structure*

The orthorhombic TiNiSi structure, although substantially different from the ZrRuSi structure discussed earlier, is built from the same $MM'X$ subcell and contains undistorted M-M' chains. The structure has layers which are filled with *both* M and M' atoms and these layers are all equivalent. The important features of this structure and their effect on superconducting T_c have been discussed earlier with reference to ZrRuP (Subba Rao and Geetha Balakrishnan 1984).

3. Present studies

The hexagonal ZrNiAl or Fe_2P-type structure is favourable in giving rise to high T_c superconductivity in $MM'X$ pnictide phases. However, charge transfer effects and electronic density of states also do play a significant role since ZrRuSi with the ZrRuP-structure is not at all superconducting above 1·2 K. Since a large number of ternary $MM'X$ silicides are reported in the literature crystallizing with the ZrNiAl structure, we thought it would be interesting to examine the compounds MReSi, MRuSi, MRuGe (M = Nb, Ta) and a few solid solutions $(Zr_{1/2}M_{1/2})$RuSi, M = V, Nb, Ta, Mo for superconductivity. Of the above, the existence of only NbReSi and TaReSi have been reported in the literature (Yarmolyuk and Gladshevskii 1974) where it was mentioned that the phases crystallize in the ZrNiAl structure.

We have presently synthesized the above compounds in addition to the known phase ZrRuSi and find that MReSi and MRuSi (M = Nb, Ta) crystallize in the TiFeSi-structure, which is a distorted version of ZrNiAl. We discovered superconductivity in all the above four compounds but the T_c values are low ($T_c < 5$ K). The low T_c may perhaps be due to the distortion in the crystal structure. The solid solutions $(Zr_{1/2}M_{1/2})$RuSi, M = Nb, Ta retain the hexagonal ZrRuSi structure but are not superconducting above 2·2 K, a behaviour similar to ZrRuSi. We also report the electrical resistivity and Seebeck coefficient data in the range 77–300 K for a few representative compounds.

4. Experimental

4.1 *Sample preparation and characterization*

Stoichiometric proportions of the high purity elements (Zr – 99·99 % [Nuclear Fuel Complex, Hyderabad, India]; Nb – 99·8 %, V-99·5 %, Rh – 99·9 %, Ta-99·9 %,

Mo -99.9%, Ge-99.999%, Ru- 99.9% [Ventron, USA] Re- 99.99% [Cerac, UK] and Si lumps 99.5% [Ventron, USA]) were taken and melted in a d.c. arc furnace [Centorr, USA]. The arc melting was carried out on a water-cooled copper hearth under a purified and Ti-gettered argon atmosphere. Melting was done three to four times by inverting the alloy buttons to promote homogenization. The arc melted samples were then crushed, ground, pelletized and annealed at 900°C for 7–10 days in evacuated (10^{-5} Torr) and sealed quartz tubes.

. The as-cast and annealed samples were characterized by the powder x-ray diffraction technique using a Guinier camera and diffractometer (Cu-Kα radiation). Quartz was used as the internal standard. The lattice constants were obtained by least square fitting of the high angle lines.

4.2   *T_c and electrical studies*

The superconducting transition temperatures of the compounds were measured on ground and powdered portions of the as-cast and annealed samples. The measurements were made by an inductive (flux expulsion) method using a liquid He cryostat. A low frequency excitation (123 Hz) was used. High purity tin ($T_c = 3.8$ K) or niobium ($T_c = 9.2$ K) or lead ($T_c = 7.2$ K) was used as standard both for calibration of temperature as well as signal strength. Temperature was measured using a Si diode sensor with an accuracy of ± 0.05 K. The T_c values reported correspond to the midpoint of the susceptibility transition. The transition width was taken as the temperature interval between 10% and 90% of the signal during the transition.

Resistivity vs temperature studies were carried out on sintered pellets in the temperature range 100–300 K. The measurements were made by the Van der Pauw method using four point probes. The apparatus used for measurement has been described earlier (Umarji 1980). The Seebeck coefficient measurements were carried out in the range 100–300 K, on the sintered pellets with respect to copper using the apparatus previously described (Umarji 1980).

5.   Results and discussion

5.1   *Structure*

A study of the x-ray diffraction patterns obtained on the compounds synthesized showed that most of them were well defined single phase materials with the exception of the following: MRuGe, M = Nb, Ta; (Zr$_{1/2}M_{1/2}$) RuSi, M = V, Mo and Zr(Ru$_{1/2}$Rh$_{1/2}$)Si. The latter showed complex x-ray patterns and perhaps are multiphasic in the as-cast form and further studies were not made on them.

The x-ray powder patterns of MM'Si compounds (M = Nb, Ta, M' = Ru, Re) could be basically indexed to the hexagonal ZrNiAl type structure. However, additional weak lines which could not be indexed to the ZrNiAl type structure and broadening and splitting of some of the lines were observed. This has been previously observed in the case of the orthorhombic TiFeSi (Jeitschko 1970a, b) which has a superstructure based on the ZrNiAl structure. The above compounds could thus be successfully indexed to the orthorhombic TiFeSi-type structure. The compounds NbReSi and TaReSi have been previously synthesized by Yarmolyuk and Gladyshevskii (1974) and were reported to crystallize in the ZrNiAl-type hexagonal structure. Our studies, however,

Table 5. X-ray powder data on 1:1:1 silicides

(Zr₁/₂Nb₁/₂)RuSi				NbRuSi				TaReSi			
hkl	d_{obs}	d_{cal}	I_{obs}	hkl	d_{obs}	d_{cal}	I_{obs}	hkl	d_{obs}	d_{cal}	I_{obs}
100	5·686	5·710	w	{ 011 / 020	5·670	5·671 / 5·707	m	{ 011 / 020	5·775	5·741 / 5·807	m
				121	3·663	3·680	w	—	—	—	—
001	3·644	3·647	vw	—	—	—	—	—	—	—	—
110	3·349	3·297	m	{ 002 / 031	3·276	3·268 / 3·288	s	{ 002 / 031	3·336	3·303 / 3·340	s
101	3·074	3·074	s	{ 211 / 220	3·021 / 2·994	3·016 / 3·021	s / w	{ 211 / 220	2·983	2·989 / 2·998	s
200	2·851	2·855	w	{ 022 / 040	—	—	—	{ 022 / 040	2·890	2·871 / 2·903	m
111	2·443	2·446	vs	{ 202 / 231	2·439 / 2·412	2·408 / 2·416	m / vs	{ 202 / 231	2·402	2·402 / 2·417	vs
				132	2·333	2·341	vw	132	2·336	2·365	m
				310	2·314	2·325	w	—	—	—	—
201	2·246	2·248	vs	{ 222 / 240	2·218	2·218 / 2·227	vs	{ 222 / 240	2·220	2·220 / 2·235	s
				150	2·181	2·174	w				
210	2·155	2·158	vs	{ 013 / 042	2·141	2·140 / 2·149	vs	{ 013 / 042	2·183	2·163 / 2·181	s
				321	2·080	2·078	w	321	2·118	2·058	m
				330	2·052	2·014	w	330	2·044	1·999	w
				123	1·951	1·957	w	123	1·990	1·975	w
				312	1·923	1·894	w				
300	1·899	1·903	w	{ 033 / 060	1·891	1·890 / 1·902	s	{ 033 / 060	1·927	1·914	s
211	1·856	1·857	w	{ 213 / 242	1·837	1·834 / 1·840	s	{ 213 / 242	1·851	1·840 / 1·851	s
002	1·826	1·824	m	400	1·784	1·781	s	400	1·743	1·751	s
				332	1·713	1·715	w				
112	1·595	1·596	vw	{ 402 / 431	—	—	—	{ 402 / 431	1·528	1·547 / 1·550	m
				{ 422 / 440	1·509	1·508 / 1·511	m				
				{ 204 / 262	1·487	1·485 / 1·493	m	{ 204 / 262	—	—	—
				352	1·465	1·470	w				
311	1·451	1·453	m	{ 224 / 253	1·441	1·437 / 1·441	s	{ 224 / 253	1·457	1·446 / 1·454	s
				{ 044 / 080	1·417	1·418 / 1·427	m	{ 044 / 080	1·420	1·435 / 1·430	m
212	1·392	1·393	m	{ 413 / 442 / 451	1·370	1·369 / 1·371	s	{ 413 / 442 / 451	1·361	1·361 / 1·365	s

m—medium; *s*—strong; *w*—weak; *v*—very.

clearly show that they crystallize in the orthorhombic TiFeSi structure, the superstructure lines being clearly visible in the Guinier powder patterns. As the superstructure lines of the TiFeSi structure are quite weak, it might be possible that some of the ternary phases, reported in literature to be isotypic with the ZrNiAl structure on the basis of a Debye-Scherrer x-ray pattern, actually crystallize with the TiFeSi structure. The compounds crystallizing with the TiFeSi structure were annealed at 900°C for one week to see if they reverted to the hexagonal structure. The x-ray powder patterns after annealing, however, showed that they still retained the orthorhombic TiFeSi structure. No impurity phases were found in the samples either before or after annealing. The x-ray Guinier data are given in table 5 and the LSQ fit lattice parameters are presented in table 6.

The x-ray patterns of the solid solutions, $(Zr_{1/2}M_{1/2})$ RuSi ($M =$ Nb, Ta) showed that they crystallize with the undistorted ZrNiAl-structure. The ZrRuSi presently synthesized was also found to crystallize in the hexagonal ZrNiAl structures as reported in the literature (Johnson and Jeitschko 1972). The Guinier x-ray powder data and lattice parameters for $(Zr_{1/2}Nb_{1/2})$RuSi (hexagonal) is given in tables 5 and 6.

5.2 *Physical properties*

The compounds are black in colour and stable towards exposure to air and moisture. They can be easily powdered and cold pressed to pellets for annealing purposes.

5.2a *Superconductivity*: The low frequency a.c. susceptibility technique definitely established superconductivity in the four compounds, MRuSi and MReSi ($M =$ Nb, Ta). The T_c values range from 2·7 to 5·1 K (table 6). The transitions are complete in almost all cases with the transition widths (ΔT) ranging from 0·5 to 1 K. Annealed samples showed slightly lower transition temperatures, by about 0·2–0·4 K, but the nature of the transition (sharpness) remained unchanged. Figure 3 shows the

Table 6. Crystal, T_c and electrical data of ternary silicides $MM'Si$

Compound	Lattice parameters (± 0.005 Å)			ρ_{300K} ($\times 10^{-3}$ ohm cm)	α_{300K} $\mu V/K$	T_c, K[‡]
	a	*b*	*c*			
Hexagonal ZrRuSi-type						
ZrRuSi	6·660		3·655	1·6	−8·4	*
$Zr_{0.5}Nb_{0.5}$RuSi	6·593		3·647	2·0	−4·8	**
$Zr_{0.5}Ta_{0.5}$RuSi	6·586		3·651	—	—	—
Orthorhombic TiFeSi-type						
NbRuSi	7·123	11·413	6·535	—	−4·3	2·65
TaRuSi	7·222	11·111	6·482	3·3	−7·5	3·15
NbReSi	7·070	11·442	6·606	—	—	5·1
TaReSi	7·002	11·614	6·605	—	—	4·4

*Not superconducting above 1·2 K (Johnston and Braun 1982; Barz *et al* 1980); **Not superconducting above 2·2 K; ‡Data on the as cast unannealed samples. T_c values showed slight decrease on annealing (see text and figure 3)
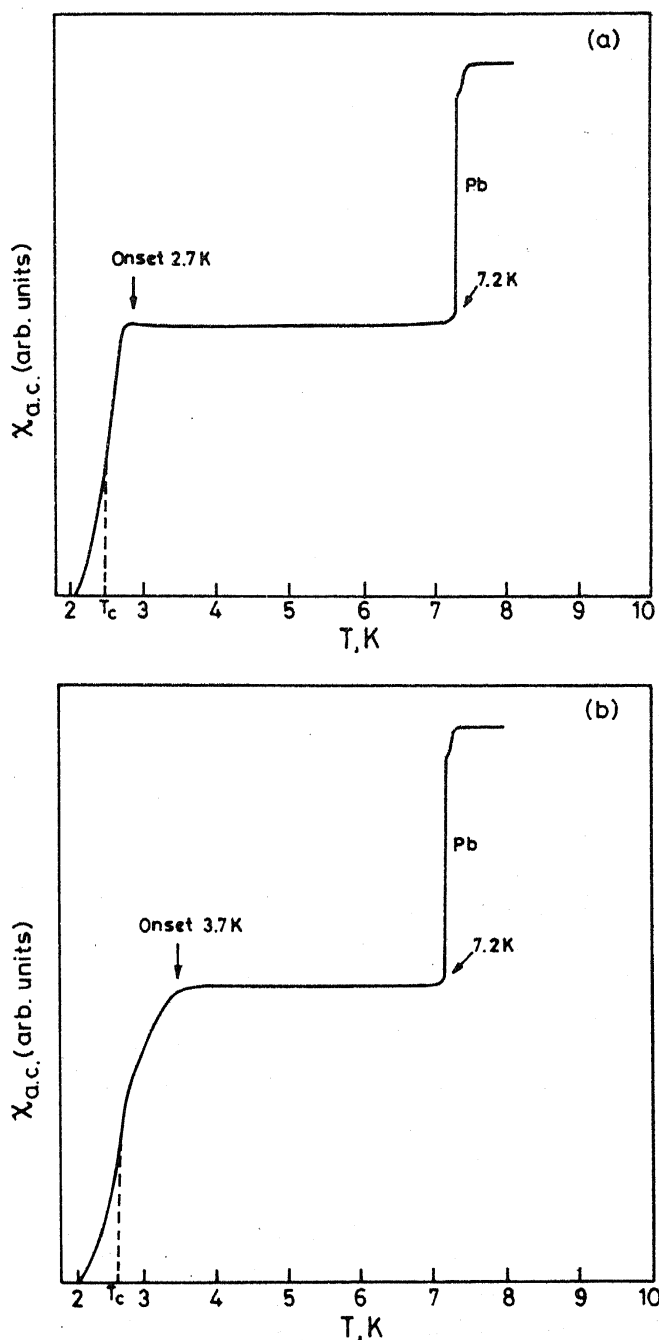
Figure 3. Superconducting transitions of (a) NbRuSi and (b) TaRuSi measured by the a.c. susceptibility method (123 Hz). Data are for the annealed samples. T_{onset} values are indicated. T_c values are 2·46 and 2·68 K respectively. The transition of Pb-metal ($T_c = 7·2$ K), used as the internal standard is also shown.

superconductivity transitions in NbRuSi and TaRuSi after annealing. Lead ($T_c = 7·2$ K) was used as the internal standard. The compound $(Zr_{1/2}Nb_{1/2})RuSi$ was not found to be superconducting upto 2·2 K, our lowest attainable temperature.

The presently observed low T_c values in $MM'Si$ ($M = $ Nb, Ta; $M' = $ Ru, Re) are perhaps the result of the orthorhombic TiFeSi-structure adopted by these compounds rather than the favoured hexagonal ZrRuSi structure. In fact Meisner (1983) found that

HfRuAs remained normal down to 1 K when crystallized in the TiFeSi-structure whereas the same compound had a T_c of 4·9–4·4 K when crystallized in the hexagonal ZrRuSi structure. Thus, the TiFeSi-structure does not appear to be conducive to high T_c. Since TiFeSi is closely related to the hexagonal ZrRuSi structure, we do not expect large changes in the electronic band structure of HfRuAs crystallizing in the two crystallographic modifications and only the changes in the electron-phonon interactions must be responsible for the observed behaviour in HfRuAs. Similar arguments can be applied for the silicides presently studied.

The fact that MRuSi and MReSi, M = Nb, Ta are superconducting, whereas ZrRuSi is normal shows that the charge transfer from Nb or Ta to Ru and Re is definitely affecting the band structure and increasing the density of states at the Fermi level (E_F). *A priori* it is not possible to indicate whether a peak exists in the density of states at E_F in NbRuSi or NbReSi. Detailed band structure calculations and xps studies may throw light on this. Lack of superconductivity in $(Zr_{1/2}Nb_{1/2})$RuSi with the hexagonal structure above 2·2 K indicates that either T_c is lower than 2·2 K or that the charge transfer from Nb is not sufficient to change the band structure of ZrRuSi and increase the density of states at the Fermi level.

5.2b *Resistivity and Seebeck coefficient*: The electrical resistivities and Seebeck coefficients of a few representative samples, namely, ZrRuSi, TaRuSi, $(Zr_{1/2}Nb_{1/2})$RuSi, have been measured in the temperature range 100–300 K. The results are shown in figures 4 and 5 and table 6. A linear increase in the resistivity with increasing temperature is observed for pure compounds. The resistivity is almost temperature independent for $(Zr_{1/2}Nb_{1/2})$RuSi unlike those of the other two compounds. Due to the electron transfer from Ta or Nb to Ru, a larger concentration of conduction electrons is expected in the case of TaRuSi and $(Zr_{1/2}Nb_{1/2})$RuSi as compared to ZrRuSi and hence these compounds are expected to be more metallic. The room temperature electrical resistivities of the three compounds are, however, almost comparable despite their differences in electron concentration, the difference lying only in the temperature dependence of the electrical resistivities.

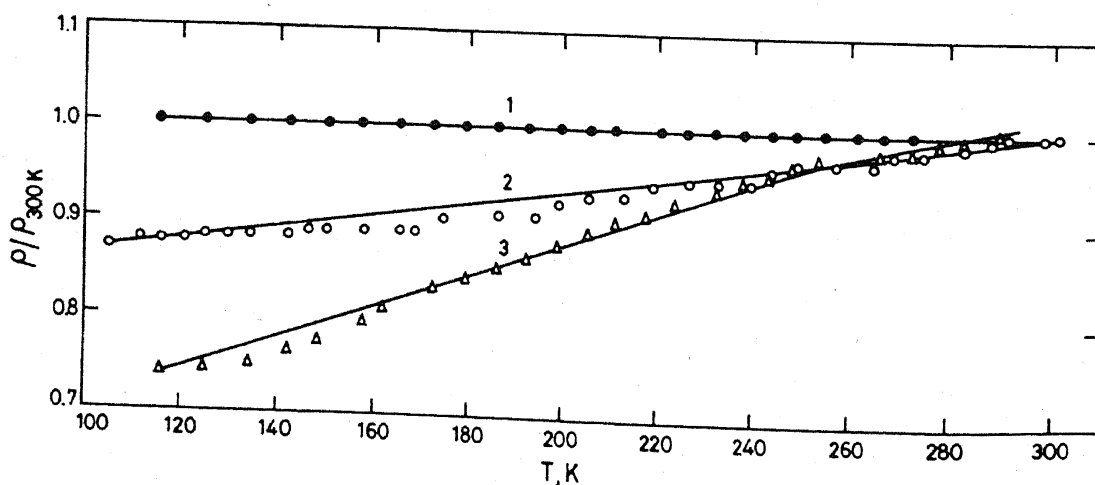All the compounds studied show negative values of Seebeck coefficient (α) ranging

Figure 4. Normalised resistivity *vs* temperature plots for the ternary silicides (1. $Zr_{0.5}Nb_{0.5}$RuSi; 2. TaRuSi; 3. ZrRuSi).
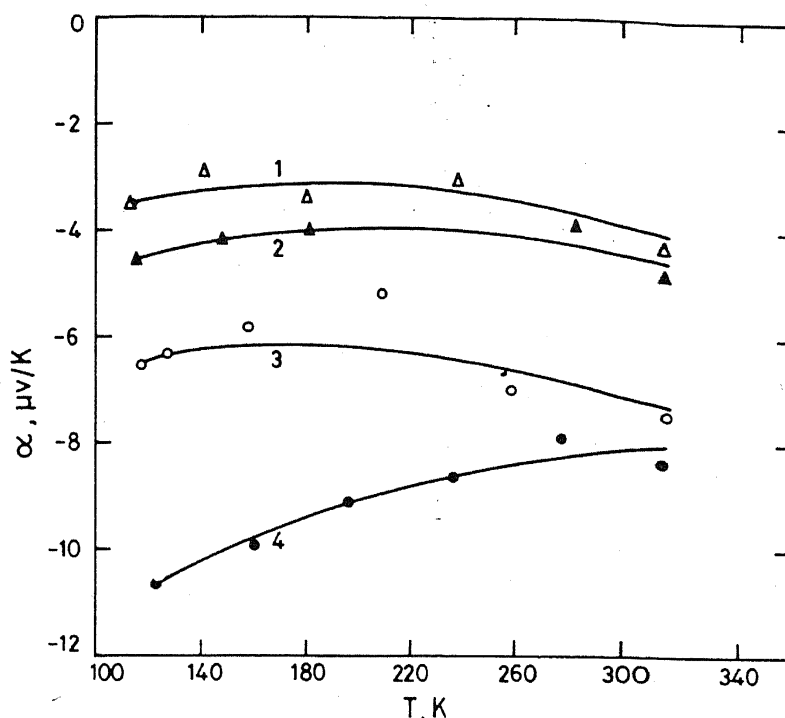
Figure 5. Seebeck coefficient *vs* temperature plots for the silicides MM'Si (1. NbRuSi; 2. $Zr_{0.5}Nb_{0.5}$RuSi; 3. TaRuSi; 4. ZrRuSi).

from 3 to 9 μV/K at room temperature and almost similar temperature dependence indicating electrons as the majority charge carriers. The conduction bands of TaRuSi, NbRuSi and $(Zr_{1/2}Nb_{1/2})$RuSi are expected to be more filled than for ZrRuSi due to an increase in the charge transfer. This is also brought out by the fact that the values of α for NbRuSi, $(Zr_{1/2}Nb_{1/2})$RuSi and TaRuSi are less negative than that of ZrRuSi.

6. Conclusions

Of the series of ternary equiatomic silicides MM'Si ($M = $ Zr, Nb, Ta; $M' = $ Ru, Re) synthesized, the compounds MRuSi and MReSi ($M = $ Nb, Ta) adopt the orthorhombic TiFeSi structure and the compounds ZrRuSi and $(Zr_{1/2}M_{1/2})$RuSi ($M = $ Nb, Ta) adopt the ZrNiAl structure. All compounds are metallic and exhibit negative Seebeck coefficients. The compounds MRuSi and MReSi ($M = $ Nb, Ta) are superconducting with T_c between 2·7 and 5·1 K. The low values of T_c are perhaps due to the fact that they adopt the TiFeSi structure rather than the favourable ZrNiAl structure. However, it is noteworthy that they indeed exhibit superconductivity as expected indicating that charge transfer plays an important role in determining the superconducting properties in the 1:1:1 ternary systems.

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