

**CRYSTAL GROWTH AND CHARACTERIZATION OF MT_2Si_2 TERNARY INTERMETALLICS
($M = U, RE$ AND $T = 3d, 4d, 5d$ TRANSITION METALS)**

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Bulk single crystals of the ternary intermetallic compounds UT_2Si_2 ($T = Ni, Pd, Pt$ and Ru), LaT_2Si_2 ($T = Pd$ and Rh) and $LuPd_2Si_2$ have been grown from the melt with a modified "tri-arc" Czochralski method. The as-grown crystals were characterized by X-ray, microprobe and chemical analyses. The measured densities are compared with the calculated densities as obtained from the lattice parameters. A detailed metallography analysis of both polycrystalline and single-crystalline samples shows that the Mt_2Si_2 intermetallics exist only in a very narrow homogeneity range and that the segregation of second phase is almost always present in polycrystalline samples and can severely mask the intrinsic properties of these materials. The effect of heat treatment on the electrical resistivity of single-crystalline URu_2Si_2 is presented, along with some preliminary results on the crystal growth of URh_2Ge_2 .

1. Introduction

The ternary compounds MT_2X_2 with $M = RE, Th$ and U , $T = 3d, 4d$ or $5d$ transition metal, and $X = Si$ or Ge have attracted a great deal of interest because of their unusual magnetic and superconducting properties [1,2]. One of these compounds, the heavy fermion system URu_2Si_2 exhibits the fascinating combination of magnetic ordering and superconductivity [3–5].

There are several reasons to grow large, bulk single crystals of MT_2X_2 compounds. Large anisotropies make the interpretation of experimental data measured on polycrystalline samples difficult or impossible, especially if preferential orientations and textures are present. The anisotropic behaviour manifests itself quite dramatically in the physical properties. The temperature dependence of magnetic susceptibility of URu_2Si_2 may serve as a typical example [3,4]. Furthermore we

have found that formation of primary and secondary precipitates in the grain and subgrain structure during the growth procedure, under near-equilibrium conditions, is substantially suppressed [6]. Such precipitates can easily mask the intrinsic physical properties of (122) series. Superconducting precipitates can form a three-dimensional network and may short-circuit the resistance of the sample as discussed for $LaRh_2Si_2$ [7]. On the other hand, the precipitates can act as a magnetic impurity which is clearly affecting the low temperature magnetic susceptibility as observed on polycrystalline compounds URu_2Si_2 [4] and $LaRh_2Si_2$ [8]. In both, the rapid increase of the low temperature magnetic susceptibility which is not observed in single crystalline samples is not an intrinsic property of (122) stoichiometry [3,7]. Finally, Palstra et al. [9] measured the overall temperature dependence of the electrical resistivity of URu_2Si_2 single crystal parallel to the a - and c -axes. The room-temperature resistivity is $330 \mu\Omega$ cm parallel to the a -axis and $170 \mu\Omega$ cm parallel to the c -axis. These values are about a factor 10 smaller than that reported by Maple et

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al. [5] and about a factor 1.5 smaller than reported by Schlabit et al. [4] on polycrystalline samples. Such differences clearly illustrate the need for well-defined homogeneous and second-phase-free single-crystalline samples to obtain reliable results on the magnetic and superconducting properties of the (122) compounds. An additional need is for extremely large single crystals for use in neutron scattering experiments to resolve the excitation spectrum [10] or the ordering of very small magnetic moments $\cong 0.01 \mu_B$ as is the case in Ru_2Si_2 [11].

We have grown several bulk single crystals of (122) ternary compounds by means of the "tri-arc" modified Czochralski method. We report here the experimental conditions for bulk single-crystal

growth of UT_2Si_2 ($T = Ni, Pd, Pt$ and Ru), LaT_2Si_2 ($T = Pd$ and Rh) and $LuPd_2Si_2$. Some preliminary results on the crystal growth and the low-temperature properties of URh_2Ge_2 are also presented. The crystal growth and characterization of CeT_2Si_2 where $T = Ni, Pd$ and Pt is described in ref. [6].

2. Crystal growth

The crystal growth of ternary compounds mentioned above was performed in a modified "tri-arc" Czochralski puller described extensively in ref. [12]. No automatic diameter control system has been applied.

Table 1
Characteristics of the growth of (122) single crystals

Compound	Suggested congruent melting temperature ($^{\circ}C$)	Vapor pressure of elements at T_m of compound (10^{-x} Torr)		Getter material	Argon pressure (Torr)	Pulling rate (mm/h)	Tip rotation rate (rpm)	Crucible rotation rate (rpm)
		Element	x					
$LaRh_2Si_2$	>1500	La	4	Ti	800	15	18	18
		Rh	6					
		Si	3					
$LaPd_2Si_2$	~1500	La	4	Ti	900	10–22	23	18
		Pd	2					
		Si	3					
$LuPd_2Si_2$	~1500	Lu	3	Ti	950	10–15	23	30
		Pd	2					
		Si	3					
UNi_2Si_2	~1500	U	6	Zr	950	15	12	15
		Ni	2					
		Si	3					
UPd_2Si_2	~1500	U	6	Zr	920	15	12	18–32
		Pd	2					
		Si	2					
UPt_2Si_2	≥ 1500	U	6	Ti	950	15	23	24
		Pt	6					
		Si	3					
URu_2Si_2	≥ 1500	U	6	U	900	10–15 ^{a)}	23 ^{a)}	18 ^{a)}
		Ru	8			10 ^{b,c)}	10 ^{b,c)}	10 ^{b,c)}
		Si	3					
URh_2Ge_2	>1200	U	8	U	800	12	23	15
		Rh	8					
		Ge	3					

^{a)} Polycrystalline as-cast seed.

^{b)} Single-crystalline seed along the a -axis.

^{c)} Single-crystalline seed along the b -axis.

Pure elements (RE, U and T) and ultrapure Si were arc-melted in a separate furnace to yield a melt of 10–30 g. An as-cast cylinder with a diameter of 3 mm and 20 mm long served as a polycrystalline tip. In the case of URu_2Si_2 oriented seeds (along the a - and c -axis, respectively) were used.

Bulk single crystals grew on the polycrystalline seed quite easily after a few millimeters so that no necking procedure was necessary. The extinction of grain boundaries in the initial stage of pulling was clearly observed by a colour TV monitoring system.

Weight losses during the growth procedure were negligible for all grown compounds as can be expected from the vapour pressure of the elements at the presumed melting temperature of the compounds. The characteristics of the growth procedure are presented in table 1.

3. Results and discussion

The main motivation for this work was to grow bulk single crystals of dimensions large enough for physical investigations. No attempt was made until now to optimize the growth parameters and starting material composition and/or the purity.

The “tri-arc”-cold crucible technique proved to be most suitable for two reasons. First, this technique allows us to reach the quite high melting temperatures of these compounds. Second, using the cold crucible avoids contamination from crucible material. Moreover, employing a continuous gettering effect in the growth atmosphere kept the contamination at the lowest level during the pulling procedure. Oxide impurities already present in the RE and U starting material were deposited on the surface of the grown crystals in the same way as described for the CeT_2Si_2 compounds [6].

Although there are no ternary phase diagrams of the (122) compounds available (except for La–Rh–Si [1] and Ce–Cu–Si [14]), nevertheless we conclude from the behaviour with respect to crystal growth that all MT_2Si_2 compounds studied melt congruently at temperatures around or higher than 1500°C.

The as-grown crystals are quite brittle and hard. They showed a tendency to fracture along the basal plane. The facetting phenomenon was ob-

served as a common feature of (122) compounds when growing the crystal. This phenomenon depends closely on the growth direction. Larger facets were formed when the growth direction is closer to the a -axis of the tetragonal crystal structure. The a -axis is also the preferential growth direction if growing on the polycrystalline seed. The facets are formed perpendicular to the c -axis. Generally, when growing along the c -axis, the crystals are more uniform and of circular cross-section than those grown out of the c -axis. This is clearly seen in fig. 1, where we show the as-grown crystal of URu_2Si_2 grown on the polycrystalline seed (a). Here the growth direction is close to the a -axis. The crystals (b) and (c) also shown in fig. 1 have been grown on a single-crystalline seed along the a - and c -axis, respectively. Further we demonstrate the ability to grow very thin “necks” by the “tri-arc” method. This is illustrated in fig. 1b where the diameter of the neck is approximately 0.3 mm. However, it should be pointed out that the stability of the solid–liquid interface of the (122) compounds is very high.

Laue pictures taken on the as-grown crystals were of rather poor quality (except for URu_2Si_2) due to the presence of impurities on the surface. However, the same pictures on as-cleaved or spark-cut surfaces showed single-grain patterns with very sharp spots for all the as-grown crystals. Light microscopy observations verified the single-grain structure and no foreign phases and/or voids were detected.

A detailed metallography analysis of the off-stoichiometric polycrystalline $LaRh_2Si_2$ [7] showed that the deviations of 1% or more from the (122) stoichiometry always resulted in segregation of a second phase with a composition according to the phase diagram [1]. Such precipitates were not detected in the as-grown crystal pulled from the stoichiometric melt [7].

In table 2 we list structure, lattice parameters, densities and the superconducting transition temperatures of the as-grown single crystals. The experimental densities agree very well with the calculated ones from the lattice parameters and indicate within experimental errors that the deviations from (122) stoichiometry are negligible in our case.

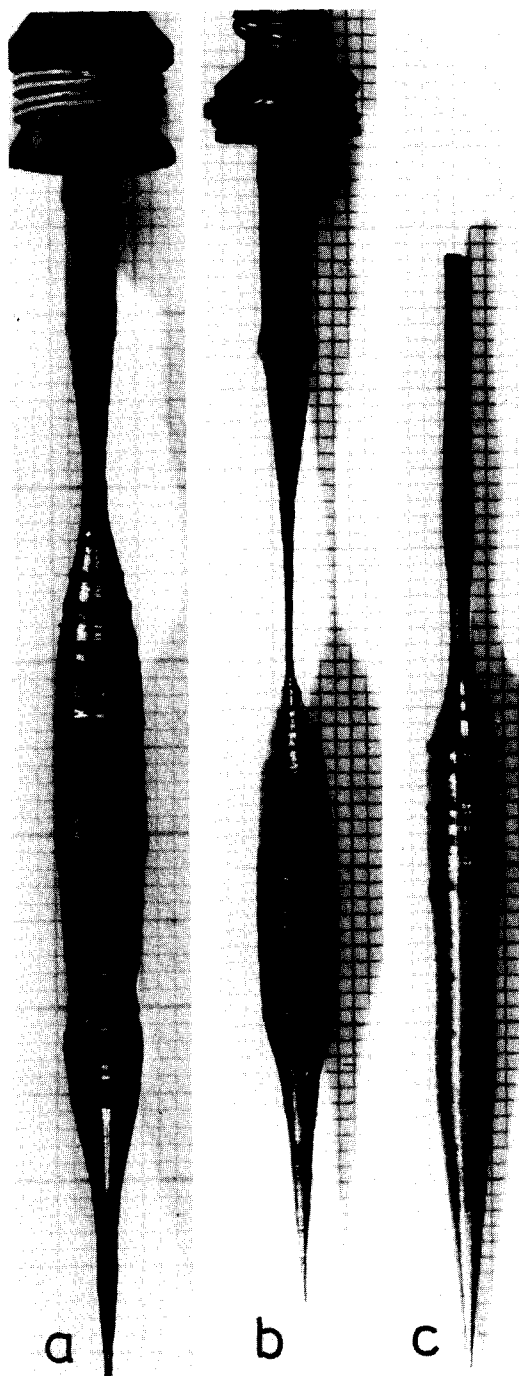


Fig. 1. The as-grown single crystal of URu_2Si_2 : (a) grown on the polycrystalline seed; (b), (c) grown on the single-crystalline seed along the a - and c -axes, respectively.

Microprobe analysis on pieces cut from the top and bottom of as-grown crystals showed an uniform composition for all compounds.

The electrical resistivity measurements performed on pieces cut from large URu_2Si_2 (120 mm length, 5–8 mm diameter) annealed single crystal are presented in table 3. Additionally, the resistivity measured on the polycrystalline samples by other authors are shown in the same table. Four main conclusions can be drawn from the electrical resistivity investigations.

(1) The electrical resistivity of URu_2Si_2 is highly anisotropic with its room-temperature value parallel to the a -axis almost twice as large as parallel to the c -axis. A detailed analysis of the anisotropic electrical resistivity measured on the unannealed URu_2Si_2 single crystal is given by Palstra et al. in ref. [9].

(2) Rather large random variations in the resistivity along the annealed crystal have been observed. Possible causes for such large variations may be due to the compositional gradients along the crystal, a result of the Czochralski method, as well as in the micro- or submicro-crystalline imperfections and nonhomogeneously distributed impurities. However, if the variations are due to the compositional gradients, they are smaller than those we can detect by our microprobe measurements. The microprobe analysis on pieces taken from the vicinity of the resistivity samples did not reveal (within experimental errors) any significant gradients in the composition. Also Laue pictures taken from several parts of the annealed crystal showed single-grain spots without a detectable mosaic spread. Nevertheless, more detailed studies on the crystalline perfection, as well as the structural investigations with respect to possible random distribution of the Ru and Si atoms in the 4(d) and 4(e) sites of the $ThCr_2Si_2$ type of structure (as described by Mayer and Yeter [15]), are necessary.

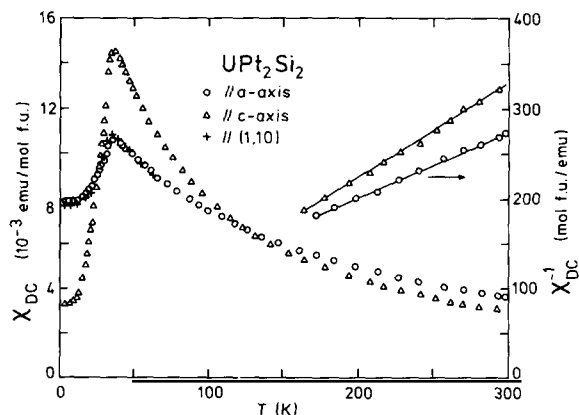
(3) The $(\rho_{300K}/\rho_{4.2K})$ increases after annealing by a factor of 1.5 to 2. This increase is mainly due to the lowering of the 4.2 K value. The room-temperature resistivity is not substantially affected by annealing. Furthermore, annealing treatments lead to increasing the superconducting transition temperature T_c . However, commensurately the width

Table 2
Structure, lattice parameters, densities and superconducting transition temperature of as-grown crystals

Compound	Structure type	Unit cell parameter (Å)		Density (g/cm ³)		T_c (K)
		<i>a</i>	<i>c</i>	Calculated	Experiment	
LaRh ₂ Si ₂	ThCr ₂ Si ₂	4.1113	10.2921	7.651	7.647	0.074 [7]
LaPd ₂ Si ₂	ThCr ₂ Si ₂	4.2778	9.8874	7.485	–	0.39 [7]
LuPd ₂ Si ₂	ThCr ₂ Si ₂	4.0868	9.8487	8.961	8.926	0.67 [7]
UNi ₂ Si ₂	ThCr ₂ Si ₂	3.9632	9.5142	9.146	9.144	–
UPd ₂ Si ₂	ThCr ₂ Si ₂	4.0775	10.0228	10.102	9.944	–
UPt ₂ Si ₂	Tetragonal primitive	4.2053	9.6955	13.253	13.234	–
UrU ₂ Si ₂	ThCr ₂ Si ₂	4.1281	9.5775	10.099	10.088	0.8 [3]
URh ₂ Ge ₂	CaBe ₂ Ge ₂ (?)	4.1547	9.7618	11.619	–	No SC down to 40 mK

Table 3
Electrical resistivity of URu₂Si₂

Sample	Distance from seed (mm)	Orientation (parallel to axis)	ρ_{300K} ($\mu\Omega$ cm)	$\rho_{4.2K}$ ($\mu\Omega$ cm)	$\rho_{300K}/\rho_{4.2K}$
Single crystal annealed (900°C/7 days)	25	<i>a</i>	356	27.3	14.05
	30	<i>c</i>	161	24	6.7
	55	<i>c</i>	166	–	–
	55	<i>a</i>	300.4	15.35	19.57
	70	<i>a</i>	376.2	24.13	15.59
	73	<i>c</i>	158	18.4	8.6
	105	<i>c</i>	179.7	–	–
Single crystal unannealed (other batch)		<i>a</i>	330	32	10.31
		<i>c</i>	170	32	5.31
Polycrystal [4] annealed (1000°C/100 h)			~ 430	~ 50	8.6
Polycrystal [5] annealed (900°C/7 days)			-2460	~ 120	20



of the transition, ΔT_c , becomes larger.

(4) There are very large differences in the resistivity values between the polycrystalline and single-crystal samples, factors of 1.5 to almost 10. The explanation for such large discrepancies probably lies in the presence of microcracks and precipitates of second which should be detectable by light microscopy on the polycrystalline samples. In order to illustrate the effects of the anisotropic

Fig. 2. Temperature dependence of the DC magnetic susceptibility of single-crystalline UPt₂Si₂ along several axes.

behaviour on the physical properties we present in fig. 2 magnetization measurements for UPt_2Si_2 along several crystallographic axes. Such anisotropic behaviour in the magnetization is common feature of all (122) compounds studied here. Additionally, we have performed low-temperature AC susceptibility measurements on single crystals of URh_2Ge_2 . No indication of superconductivity has been observed down to 40 mK.

4. Summary

We have shown that the "tri-arc" Czochralski method is suitable for the preparation of bulk single crystals of the highly reactive RE (122) and U (122) ternaries. These crystals are indispensable for the interpretation of physical measurements due to the large anisotropy effects [3,7,9,11]. To our knowledge the bulk single crystals as described here have not been grown previously.

Acknowledgements

We wish to acknowledge A.J. Dirkmaat for his help in performing some of the low-temperature measurements. This work is part of the research program of the Nederlandse Stichting voor Fundamenteel Onderzoek der Materie (FOM).

References

- [1] H.F. Braun, *J. Less-Common Metals* 100 (1984) 105.
- [2] T.T.M. Palstra, A.A. Menovsky, G.J. Nieuwenhuys and J.A. Mydosh, *J. Magnetism Magnetic Mater.* 54–57 (1986) 435.
- [3] T.T.M. Palstra, A.A. Menovsky, J. van den Berg, A.J. Dirkmaat, P.H. Kes, G.J. Nieuwenhuys and J.A. Mydosh, *Phys. Rev. Letters* 55 (1985) 2727.
- [4] W. Schlabit, J. Bauman, B. Pollit, U. Rauchswalbe, H.M. Mayer, U. Ahlheim and C.D. Bredl, *Z. Physik B62* (1986) 171.
- [5] M.B. Maple, J.W. Chen, Y. Dalichaouch, T. Kohara, C. Rossel, M.S. Torikachvili, M.W. McElfresh and J.D. Thompson, *Phys. Rev. Letters* 56 (1986) 185.
- [6] A.A. Menovsky, C.E. Snel, T.J. Gortenmulder, H.J. Tan and T.T.M. Palstra, *J. Crystal Growth* 74 (1986) 231.
- [7] T.T.M. Palstra, A.A. Menovsky, G. Lu, G.J. Nieuwenhuys, P.H. Kes and J.A. Mydosh, *Phys. Rev. B34* (1986), in press.
- [8] I. Felner and I. Nowik, *Solid State Commun.* 47 (1983) 831.
- [9] T.T.M. Palstra, A.A. Menovsky and J.A. Mydosh, *Phys. Rev. B33* (1986) 6527.
- [10] U. Walter, C.K. Loong, M. Loewenhaupt and W. Schlabit, *Phys. Rev. B33* (1986) 7875.
- [11] C. Broholm, K.J. Kjems, W.L. Buyers, T.T.M. Palstra, A.A. Menovsky and J.A. Mydosh, to be published.
- [12] A.A. Menovsky and J.J.M. Franse, *J. Crystal Growth* 65 (1983) 286.
- [13] *Material Research Catalogue* (1981) p. 4.
- [14] M. Ishikawa, H.F. Braun and J.L. Jorda, *Phys. Rev. B27* (1983) 3092.
- [15] I. Mayer and P.D. Yetor, *J. Less-Common Metals* 55 (1977) 171.