ELSEVIER

Journal of Alloys and Compounds 262–263 (1997) 238–242

Journal of ALLOYS AND COMPOUNDS

RuSi: metal-semiconductor transition by change of structure

B. Buschinger[a,*], W. Guth[a], M. Weiden[a], C. Geibel[a], F. Steglich[a], V. Vescoli[b], L. Degiorgi[b], C. Wassilew-Reul[c]

[a] *TH Darmstadt, Technische Physik, Hochschulstrasse 8, D-64289 Darmstadt, Germany*
[b] *ETH Zürich, Solid State Physics Laboratory HPF-F3, CH-8093 Zürich, Switzerland*
[c] *ESRF Grenoble, F-38043 Grenoble, France*

Abstract

RuSi has long been known to form in two modifications, i.e. CsCl-type at high temperatures, and FeSi-type at low temperatures. The transition temperature has recently been determined as 1300°C for stoichiometric material, but is strongly dependent on the exact stoichiometry. We have evaluated the structures of both phases under applied pressure of up to 40 GPa. No evidence for a pressure-induced transition was found. The bulk moduli of CsCl- and FeSi-type RuSi were determined as (215 ± 15) GPa and (255 ± 15) GPa, respectively. Transport and optical properties of both modifications have been investigated. Obviously, the CsCl-modification is metallic, whilst the FeSi-modification is a narrow-gap semiconductor with a gap of 0.2–0.3 eV. © 1997 Elsevier Science S.A.

Keywords: RuSi; Structural phase transition; Bulk moduli; Optical properties

1. Introduction

RuSi is known to form in two modifications, i.e. CsCl-type at high-temperatures (HT), and FeSi-(B20) type at low temperatures (LT) [1]. However, a phase transition between both modifications has been a matter of debate, and some workers claimed the occurrence of either phase to be determined only by stoichiometry [2]. Recently, a transition temperature of 1300°C has been measured by means of thermal expansion [3], and annealing at such high temperatures results in almost pure LT-phase polycrystals which are suitable for physical investigations.

The LT-phase of RuSi is of special interest, since it might serve as a non-magnetic reference system for the narrow-gap semiconductor FeSi [4], which is claimed as a first example of a 3d-based (instead of 4f-based) Kondo-semiconductor [5]. Measurements of the dc-resistivity, the Hall-effect, and the thermoelectric power clearly show that the LT-phase is a narrow-gap semiconductor, whilst the HT-phase is a normal metal [3].

We have now investigated the transformation behavior in some more detail, and also investigated the structural parameters under applied pressure of up to 40 GPa. In addition, the optical properties of both modifications have been investigated in a very broad spectral range.

2. Experimental

2.1. Annealing and stoichiometric studies

Recently, a transition at ~ 1300°C was observed for stoichiometric RuSi [3], but a much smaller transition temperature was reported for $Ru_{1.01}Si$. In order to examine the stoichiometry dependence of the transi-

* Corresponding author.

0925-8388/97/$17.00
PII S0925-8388(97)00389-7

tion, and also to obtain single-phase material of both modifications, the structural compositions of several samples with stoichiometries slightly deviating from the 1:1 composition were studied after certain heat treatments.

All samples were prepared by repeated arc-melting under protective Ar-atmosphere. Only samples with negligible weight loss during melting (< 0.5‰) were considered for future investigations. The samples were subjected to several annealing processes in high-vacuum. X-ray powder diffraction patterns were recorded using Cu-Kα-radiation after each annealing step. The results are collected in Table 1. In general, as-cast samples, which are rapidly cooled from temperatures well above the transition temperature, consist of a mixture of both phases, plus a small amount of Ru_2Si_3 for the samples with Si-excess. Samples rich in Ru merely consist of the high-temperature phase. This already shows that the transition is rather sluggish, and also shows that the homogeneity range of RuSi is extended for samples rich in Ru, at least up to 5% Ru-excess, but is very small for samples rich in Si. The transition temperature is strongly dependent on the exact stoichiometry: samples with the 1:1 stoichiometry show a transition around 1300°C from the low-temperature phase to the high-temperature phase, whilst samples both with Si- or Ru-excess can be transformed — at least in part — below 1000°C. This result shows that the stability range of the HT-phase increases with defects.

For the following investigations, a stoichiometric sample, which was annealed at 1300°C, was chosen as the best representative of the LT-phase, and an as-cast sample with the composition $Ru_{1.01}Si$ was chosen as representative of the HT-phase.

2.2. High pressure studies

In order to measure the bulk moduli of both modifications and to check whether a pressure-induced transition might exist, room temperature structural investigations under applied hydrostatic pressures of up to 40 GPa were carried out using synchrotron radiation at the ESRF in Grenoble. Small amounts of both FeSi- and CsCl-type RuSi were ground to very fine powder and inserted together into a diamond anvil pressure cell using a gasket with 100 μm diameter drilled hole with a methanol-ethanol 4:1-mixture as the pressure transmitter. Additionally, small pieces of ruby were inserted in order to determine the applied pressure via the shift of the fluorescence lines [6]. A silicon monochromator was used to fix a wavelength of 0.4554 Å, and several blades were used to limit the beamsize to 50 × 50 μm to ensure that only the center of the pressure cell was investigated. 2D Debye-Scherrer diffraction patterns were recorded using an image-plate system, and were integrated to obtain the conventional 1D diffraction patterns. Parts of typical diffraction patterns are depicted in Fig. 1. Starting from zero pressure, diffraction patterns were recorded at a number of pressure points up to 40 GPa, which all show reflections of both phases.

The angular position of the diffraction lines was used to evaluate the lattice parameters of both phases as a function of pressure. Below ~20 GPa, the observed lines are very sharp as hydrostatic pressure conditions are given. Above 20 GPa, the lines broaden due to pressure gradients in the cell. Unit cell volumes, normalized to the zero-pressure values, are shown for both phases in Fig. 2. The pressure dependence was fitted using the Murnaghan [7] equation of state, which yielded bulk moduli of (255 ± 15) GPa and (215 ± 15) GPa for the CsCl-type and the FeSi-type material, respectively. At all investigated pressures, the relative intensities of the reflections of both phases remained essentially unchanged, thus showing that a pressure-induced transition amongst the two phases is absent up to 40 GPa. However, the X-ray density of CsCl-type material is 5% larger than that of FeSi-type material at ambient pressure (8.70 g/cm^3 compared

Table 1
Composition of different RuSi-samples after certain heat treatments as obtained from the relative intensities in the X-ray diffraction patterns. All annealing procedures were carried out for 120 h in a vacuum state $p < 10^{-6}$ mbar, and were followed by a slow cooling

Nominal	As cast	1000°C	1100°C	1200°C	1300°C
RuSi	70% LT, 30% HT				98% LT, 2% HT
$RuSi_{1.05}$	75% LT, 20% HT, 5% Ru_2Si_3			95% LT, 5% Ru_2Si_3	
$RuSi_{1.005}$	75% LT, 22% HT, 3% Ru_2Si_3	95% HT, 2% LT, 3% Ru_2Si_3	97% HT, 3% Ru_2Si_3	97% HT, 3% Ru_2Si_3	75% LT, 22% HT, 3% Ru_2Si_3
$Ru_{1.005}Si$	100% HT	70% LT, 30% HT	40% LT, 60% HT		
$Ru_{1.01}Si$	100% HT	80% LT, 20% HT			
$Ru_{1.05}Si$	100% HT				
$Ru_{1.1}Si$	98% HT, 2%?				

LT, low-temperature phase; HT, high-temperature phase; ?, unidentified impurity phases.

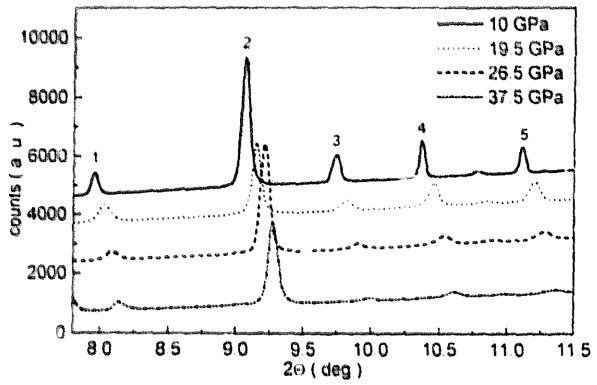

Fig. 1. Low-angle part of typical X-ray diffraction patterns of CsCl- and FeSi-type RuSi, obtained at 10, 19.5, 26.5, and 37.5 GPa, as integrated from the original 2D-imageplate data. (1): [110], (3): [111], (5): [200] reflection of FeSi-type RuSi, (2): [100] reflection of CsCl-type RuSi, (4): reflection from ruby.

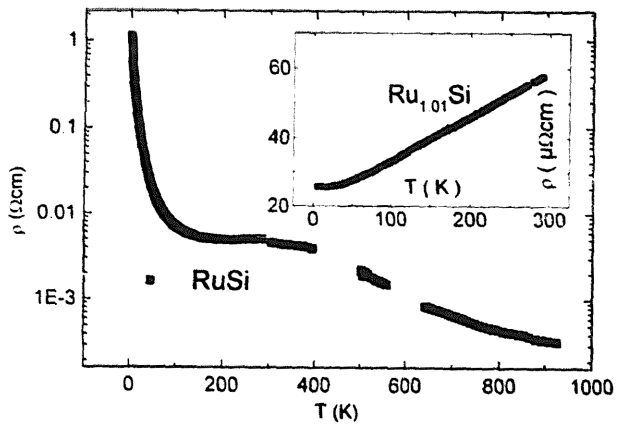

Fig. 3. Resistivity of RuSi vs. T, measured between 2 K and 900 K. Inset shows resistivity of $Ru_{1.01}Si$ in the temperature range $4 < T < 300$ K.

to 8.28 g/cm^3), and with applied pressure this difference is only moderately reduced to, e.g., 3.9% at 30 GPa. This implies that the LT phase gets stabilized, but a pressure-induced transition would only occur at extremely high pressure.

2.3. Transport and magnetic properties

For samples of both the CsCl- and of the FeSi-type, resistivity and magnetic susceptibility measurements have been carried out in the temperature ranges $2 < T < 900$ K and $2 < T < 350$ K, respectively. Magnetic measurements show small diamagnetic susceptibilities for the FeSi-type modification.

Resistivity data (Fig. 3) clearly show a conventional metallic behavior for the CsCl-type samples with a monotonic increase from a low temperature residual resistivity of ~ 20 $\mu\Omega$ cm up to 60 $\mu\Omega$ cm at 300 K.

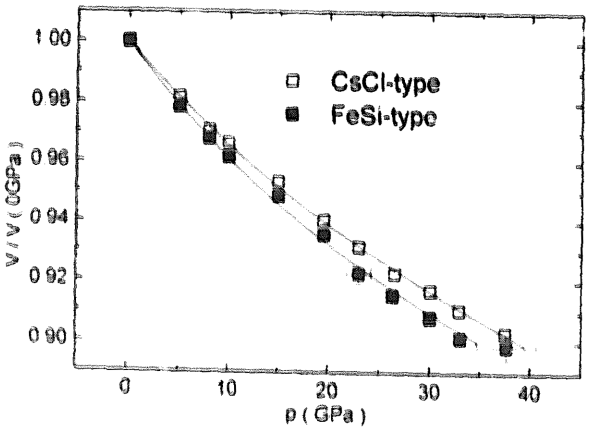

Fig. 2. Unit cell volumes normalized to the respective zero pressure values of CsCl-type (open squares) and FeSi-type (filled squares) RuSi at room temperature and at pressures from 0 to 40 GPa. Solid lines are fits according to the Murnaghan equation of state, with fit parameters $B_0 = 255$ GPa, $B_0' = 6.71$ for CsCl-type, and $B_0 = 215$ GPa, $B_0' = 7.63$ for FeSi-type RuSi.

By contrast, the resistivity of FeSi-type samples is up to five orders of magnitude larger at 2 K and decreases in a semi-conductor like manner to ~ 300 $\mu\Omega$ cm at 900 K. However, the resistance behavior shows different regimes due to the crossover from intrinsic to extrinsic conduction mechanism. At temperatures above 500 K, the resistivity follows an activated behavior, i.e. $\ln \rho \propto \Delta/2k_BT$, with a gap width of ~ 3600 K. Around room temperature, the resistivity levels off due to change from intrinsic to extrinsic conduction. At lower temperatures the resistivity again shows an activated behavior, but with a much smaller gap width of ~ 100 K. However, this activated behavior only holds down to ~ 50 K and, at still lower temperatures, a crossover to a hopping-type conductivity is obvious from the observed $\ln \rho \propto T^{1/4}$-behavior. Such power-laws are commonly ascribed to variable-range hopping (VRH) [8]. The crossover to hopping-type transport is also obvious from the drastic decrease of the mobility below 50 K [3].

2.4. Optical properties

Optical investigations revealed to be a powerful experimental tool in the case of the 3d-based transition metal monosilicides FeSi [9,10]. Thus, we have performed optical reflectivity measurements on RuSi over a very broad spectral range, extending from the far-infrared (FIR) up to the ultraviolet. The details about the experiment can be found elsewhere [10]. Fig. 4a and Fig. 5a display the reflectivity $R(\omega)$ of RuSi (FeSi-type) at 300, 100, 50 and 6 K and of $Ru_{1.01}Si$ (CsCl-type) at 300 and 6 K, respectively, over the whole measured spectral range. The corresponding real parts of the optical conductivity $\sigma(\omega)$ are shown in Fig. 4b and Fig. 5b. This latter quantity is obtained by performing the Kramers Kronig transformation on the reflectivity spectra [10]. The insets are

an enlargement of the FIR spectral range. In both $R(\omega)$ and $\sigma(\omega)$ we immediately remark a rather important temperature dependence in RuSi, which is however absent in $Ru_{1.01}Si$. This latter compound presents indeed a typical metallic and apparently temperature-independent behavior, characterized by the Drude-like component in the excitation spectrum. On the other hand, in RuSi the reflectivity decreases in FIR with decreasing temperature, manifesting the progressive disappearance of spectral weight associated with the free charge carriers. This can also be immediately recognized in $\sigma(\omega)$ (see inset of Fig. 4b), where its dc limit decreases with decreasing temperature in agreement with the dc transport data. In the spectral range from the mid-infrared up to about 1 eV there is another important temperature dependence which is particularly manifested in $R(\omega)$ (Fig. 4a). In terms of $\sigma(\omega)$, it corresponds to the huge absorption

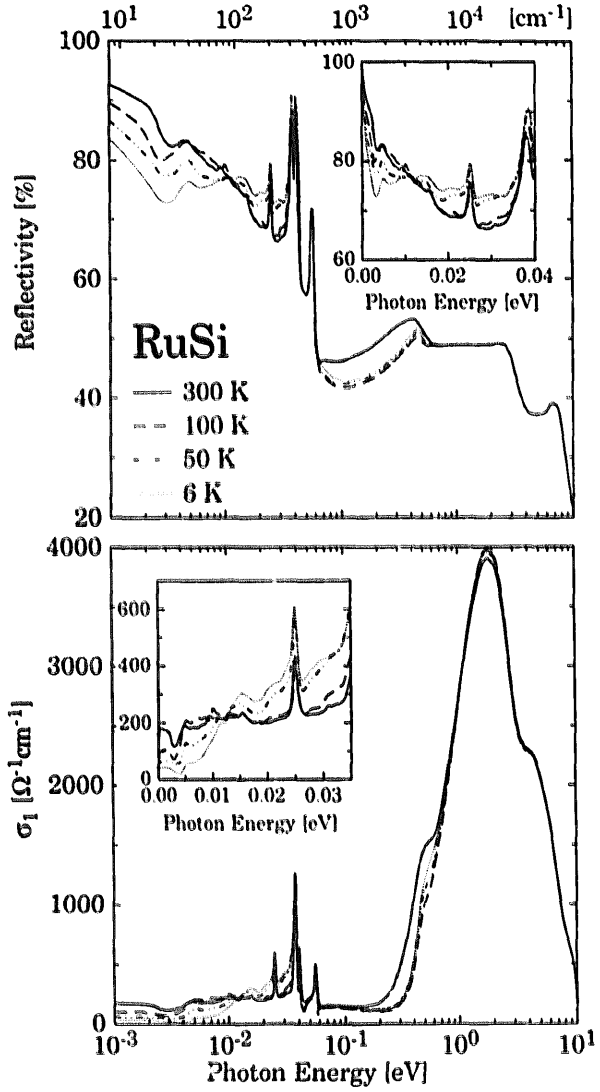

Fig. 4. (a) Reflectivity and (b) real part of the optical conductivity of RuSi. The insets display an enlargement of the FIR spectral range.

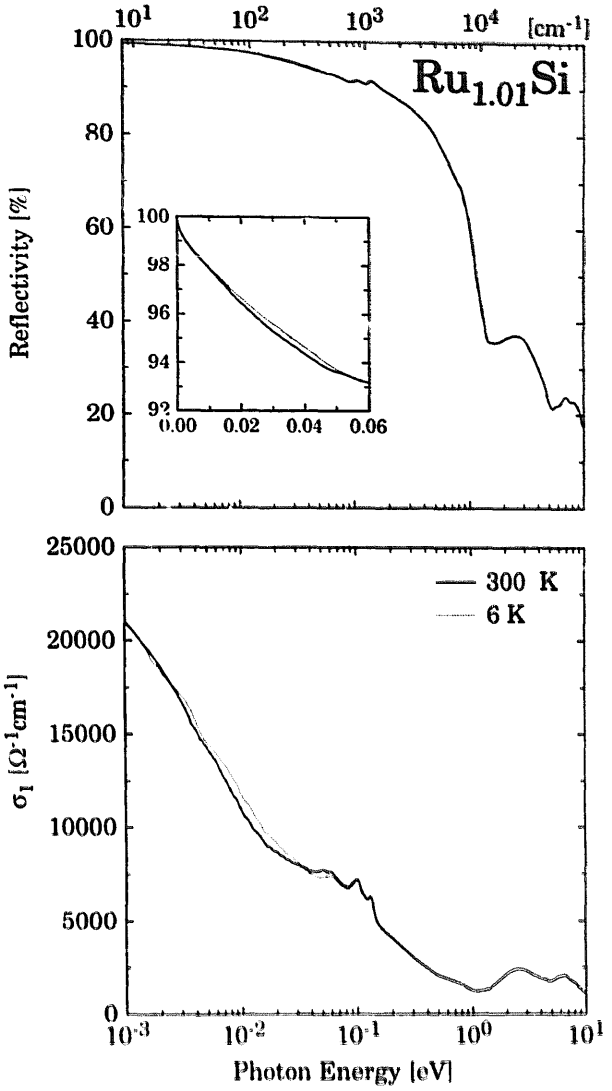

Fig. 5. (a) Reflectivity and (b) real part of the optical conductivity of $Ru_{1.01}Si$. The inset displays an enlargement of the FIR reflectivity.

at about 1.5 eV, which has an onset already near 0.2–0.3 eV. In addition, the spectra are characterized by several sharp absorptions between 200 and 600 cm^{-1}, which are probably due to lattice phonon modes. The dynamics of the charge excitation spectrum in RuSi suggest a scenario where a narrow semiconducting gap is already opened at 300 K, corresponding to the huge absorption with onset in the 0.2–0.3 eV spectral range. The residual and very small amount of spectral weight at low frequencies, which is ascribed to the free charge carriers contribution, could be mostly provided from the small amount of metallic CsCl-type RuSi. In this respect, RuSi is a poor metal and at 300 K its electrodynamic response is dominated by the pseudogap-like feature peaked around 1 eV. By lowering the temperature, RuSi changes to a true insulator, displaying moreover a new absorption

(acting as background to the lattice modes) around 200 cm^{-1}. This latter feature could be associated with the gap of the further activated behavior established at low temperatures in the transport properties. The general trend of the optical properties in RuSi is, however, different from what has been found in FeSi, for which metallic behavior was inferred at 300 K and the narrow semiconducting gap was found to open progressively below room temperature [9,10]. Further investigations are in progress in order to completely understand the electrodynamics and to reveal the nature of and the role played by correlations in RuSi.

3. Summary

We have investigated the stoichiometry dependence of the structural phase transition temperature of RuSi, and found a strong decrease from 1300°C for the pure compound to below 1000°C both with small Si- and Ru-excess. This shows that the HT phase gets stabilized by slight deviations from 1:1 stoichiometry. The homogeneity range extends up to 5% Ru excess, but only to very small Si-excess.

The evaluation of the high-pressure structural data of both phases gives no evidence for a pressure-dependent phase transition, and yields bulk moduli of (215 ± 15) GPa and (255 ± 15) GPa for CsCl- and FeSi-type RuSi, respectively.

Transport and optical properties clearly show that the HT-modification of RuSi is a simple metal, whilst the LT-modification is a narrow-gap semiconductor with a gap of ≈0.2–0.3 eV. However, physical properties of the samples investigated are strongly influenced by the remaining HT-phase impurities, and thus resemble those of heavily doped semiconductors.

Acknowledgements

Work at the ESRF was kindly assisted by Dr. M. Kunz, beamline scientist on ID30. Two of us (V.V. and L.D.) wish to thank Mr. J. Müller for technical assistance and the Swiss National Foundation for Scientific Research for financial support. Work in Darmstadt was financially supported in part by the SFB 252 Darmstadt/Frankfurt/Mainz, and by the BMBF grant No. 13N6608/1.

References

[1] J.H. Buddery, A.J.E. Welch, Nature 167 (1951) 362.
[2] K. Göransson, I. Engström, B. Noläng, J. Alloys Comp. 219 (1995) 107.
[3] B. Buschinger, C. Geibel, J. Diehl, M. Weiden, W. Guth, A. Wildbrett, S. Horn, F. Steglich, J. Alloys Comp. (in press).
[4] V. Jaccarino, G.K. Wertheim, J.H. Wernick, L.R. Walker, S. Arajs, Phys. Rev. 160 (1967) 476.
[5] D. Mandrus, J.L. Sarrao, A. Migliori, J.D. Thompson, Z. Fisk, Phys. Rev. B51 (1995) 4763.
[6] H.K. Mao, P.M. Bell, J.W. Shaner, D.J. Steinberg, J. Appl. Phys. 49 (1978) 376.
[7] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 30 (1944) 244.
[8] N.F. Mott, Metal-Insulator Transitions, Taylor and Francis, London, 1974.
[9] Z. Schlesinger, Z. Fisk, H.T. Zhang, M.B. Maple, J.F. DiTusa, G. Aeppli, Phys. Rev. Lett. 71 (1993) 1748.
[10] L. Degiorgi, M.B. Hunt, H.R. Ott, et al., Europhys. Lett. 28 (1994) 341.