# Investigations on Chemical Vapour Transport of Intermetallic Phases in the System Co/Fe/Si

**R. Boldt, W. Reichelt*, O. Bosholm, and H. Oppermann**

Dresden, Institut für Anorganische Chemie der Technischen Universität

Received August 21st, 2002.

**Abstract**. The ternary phases existing on the quasi binary section CoSi/FeSi and $CoSi_2$/β-$FeSi_2$ have been investigated by solid state reactions and chemical transport. The solid solution serie $Co_xFe_{1-x}Si$ can be described as a regular solution. The transport behaviour calculated is in good agreement with the experiments. The phases have been characterized by X-ray powder diffraction, EDX and ICP-OES. The temperature dependence of the resistivity has been measured from 20 K up to room temperature on single crystals.

**Keywords:** Ternary silicides; Chemical transport; Mixed crystals; Resistivity measurements

# Untersuchungen zum chemischen Transport intermetallischer Phasen im System Co/Fe/Si

**Inhaltsübersicht.** Im System Co/Fe/Si wurden die existierenden intermetallischen Verbindungen auf den quasibinären Schnitten FeSi/CoSi und β-$FeSi_2$/$CoSi_2$ ermittelt und deren chemisches Transportverhalten untersucht. Die thermodynamische Beschreibung der Mischkristallreihe $Co_xFe_{1-x}Si$ als reguläre Lösung beschreibt das experimentell beobachtete Transportverhalten hinreichend gut. Die erhaltenen Phasen wurden mittels Röntgenbeugung, ESMA und ICP-OES untersucht. An Einkristallen wurden elektrische Leitfähigkeitsmessungen von 20 K bis Raumtemperatur durchgeführt.

## 1 Introduction

The preparation of intermetallic phases as a phase-pure polycrystalline material and as single crystals is published only for a few systems so far. Both the reactivity and the equilibrium conditions are largely unknown for the system Co/Fe/Si. Therefore, systematical investigations are necessary concerning the exact composition of phases and the coexistence relations between them. Using the experiences on preparation of the binary systems Fe-Si and CoSi [1, 2], both solid state reactions and chemical vapour transport with $I_2$ as transport agent should by used for defined preparation in the quasi-binary systems CoSi−FeSi and $CoSi_2$−β-$FeSi_2$. Looking for homogeneity ranges, mixtures of coexisting phases should be investigated. The exact composition of the phases has been analysed by X-ray diffraction, EDX and ICP-OES.

A computer controlled transport balance is used for continuously measuring rates of transport in closed ampoules.

## 2 The System Co/Fe/Si

Two series of mixed crystals are known in the system Co/Fe/Si, one between CoSi and FeSi, the other between $CoSi_2$ and β-$FeSi_2$. The two binary compounds CoSi and FeSi crystallize in the cubic system in space group $P2_13$ (No.198) and form a complete solid-solution series. $CoSi_2$ crystallizes in the $CaF_2$-structure type (cubic space group $Fm\bar{3}m$, No. 225). $FeSi_2$ exists in two modifications: the β-phase up to 1255 K (orthorhombic space group Cmca, No. 64), the α-phase is stable from 1210 K to 1493 K ($FeSi_{2.43}$, tetragonal space group P4/mmm, No.123). Both α- and β-$FeSi_2$ coexist between 1210 K and 1255 K. Figure 1 shows an isothermal section of the system using data from the literature [3, 4].

The mutual solubility of $CoSi_2$ and β-$FeSi_2$ is limited [3, 5].

## 3 Synthesis and Characterization of the Ternary Phases

Powders of Fe, Si, and Co with a purity of 99.95 % have been used for preparation.

To make ternary phases exist, appropriate mixtures of powders were placed together with small amounts of $I_2$ (0.5-1 mg, mineralisator) in a silica ampoule. The ampoules have been evacuated, sealed off and tempered at 1173 K for about 10 days.

---

* Doz. Dr. W. Reichelt
Institut für Anorganische Chemie
der Technischen Universität
Mommsenstraße 13
D-01062 Dresden
FAX: 0351/463-37287
E-mail: werner.reichelt@chemie.tu-dresden.de

**DOI: 10.1002/zaac.200300117**

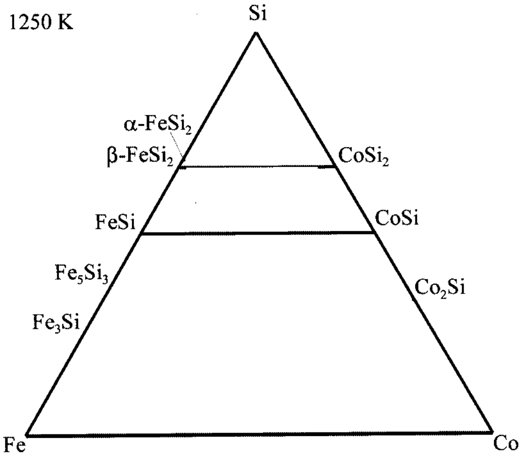

**Fig. 1** Isothermal section of the system Co-Fe-Si according to literature data [3–5]

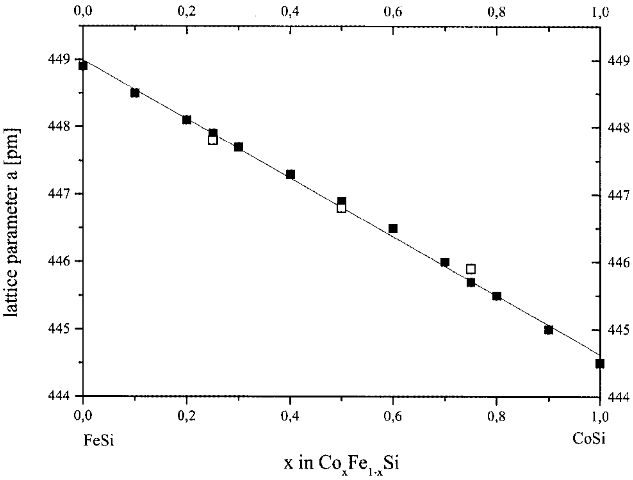

**Fig. 2** Course of the lattice constants for the mixed crystals $Co_xFe_{1-x}Si$

### 3.1 *The system CoSi/FeSi*

The samples prepared on the quasi binary line CoSi/FeSi have been characterized by X-ray diffraction. The compounds $Co_xFe_{1-x}Si$ were pure phase. No traces of other compounds could be detected. The powder patterns were refined using the Rietveld-method and the lattice parameter a were calculated for the cubic unit cell. Figure 2 shows the course of the lattice constants for $Co_xFe_{1-x}Si$. The lattice constants change about linear in accord with Vegard's rule. The expected and in literature described complete solid solutions [5] are confirmed.

In the literature [4], homogeneity ranges for $CoSi_{1\pm y}$ and for $FeSi_{1\pm y}$ are indicated. Therefore, it is likely to assume an analogous homogeneity range for the solid solution with respect to the silicium content. The assumed range for $Co_xFe_{1-x}Si_{1\pm y}$ is gray colored in Figure 3. The phase ranges of $CoSi_{1\pm y}$ and $FeSi_{1\pm y}$ could be extracted from the binary phase diagrams [4].

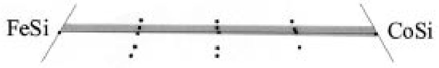

**Fig. 3** Range of $Co_xFe_{1-x}Si_{1\pm y}$ mixed crystals

**Table 1** Phase analysis and lattice parameter in the Co-Fe-Si system after solid state reaction with reactive gas phase ($I_2$)
MK1 = mixed crystal $Co_xFe_{1-x}Si_{1\pm y}$

| Initial composition | Phases in equilibrium | Lattice parameter/pm |
|---|---|---|
| $Co_{0.25}Fe_{0.75}Si_{0.85}$ | MK1 + $Fe_3Si$ + $Fe_5Si_3$ | |
| $Co_{0.25}Fe_{0.75}Si_{0.9}$ | MK1 | a = 447,8 |
| $Co_{0.25}Fe_{0.75}Si_{1.0}$ | MK1 | a = 447,9 |
| $Co_{0.25}Fe_{0.75}Si_{1.05}$ | MK1 + β-$FeSi_2$ | |
| $Co_{0.25}Fe_{0.75}Si_{1.1}$ | MK1 + β-$FeSi_2$ + $CoSi_2$ | |
| $Co_{0.5}Fe_{0.5}Si_{0.85}$ | MK1 + $Co_2Si$ | |
| $Co_{0.5}Fe_{0.5}Si_{0.9}$ | MK1 | a = 446,8 |
| $Co_{0.5}Fe_{0.5}Si_{1.0}$ | MK1 | a = 446,9 |
| $Co_{0.5}Fe_{0.5}Si_{1.02}$ | MK1 + $CoSi_2$ | |
| $Co_{0.5}Fe_{0.5}Si_{1.1}$ | MK1 + $CoSi_2$ | |
| $Co_{0.75}Fe_{0.25}Si_{0.9}$ | MK1 + $Co_2Si$ | |
| $Co_{0.75}Fe_{0.25}Si_{1.0}$ | MK1 | a = 445,7 |
| $Co_{0.75}Fe_{0.25}Si_{1.02}$ | MK1 | a = 445,9 |
| $Co_{0.75}Fe_{0.25}Si_{1.1}$ | MK1 + $CoSi_2$ | |

To investigate the real homogeneity range of $Co_xFe_{1-x}Si_{1\pm y}$, samples with the same Co/Fe ratio and different amounts of silicon have been prepared as described before. The results of phase analysis obtained by X-ray are shown in Table 1 and Figure 3, respectively. Single phase samples are marked by crosses, see also Table 1 (MK1). The results show the cobalt rich part in good agreement with the range assumed. At the iron rich part the homogeneity range is shifted to silicon poor regions and possibly larger then assumed. To obtain more exact results further investigations are necessary. The coexisting phases are in agreement with the phase diagram, except for the observation of MK1+ $Fe_3Si$ and $Fe_5Si_3$ (Fig. 1). No equilibrium could be reached in the last case. The powder pattern of MK1 also shows a shift with variation of the silicon content. The resulting lattice constants are also given by unfilled squares in Figure 2.

### 3.2 *The system $CoSi_2$/β-$FeSi_2$*

*Wittmann* et al. [5] have investigated the mutual solubility of some disilicides on molten samples. They observed that the solubility of $CoSi_2$ and β-$FeSi_2$ is very limited; $CoSi_2$ dissolves 6 Mol% $FeSi_2$, $FeSi_2$ dissolves 1 Mol% $CoSi_2$ [5].

We could prepare single phase ternary compounds by solid state reactions only on the cobalt-rich side in regions between $CoSi_2$ until $Co_{0.93}Fe_{0.07}Si_2$ (MK2). On the iron rich side multiphase samples have always been found. The X-ray pattern of the prepared disilicides (MK2) have been refined by the Rietveld method and the lattice parameter could be

**Table 2** Phase analysis and lattice parameter in the Co-Fe-Si system after solid state reaction with reactive gas phase ($I_2$)
MK2 = mixed crystal $Co_xFe_{1-x}Si_2$

| Initial composition | Phases in equilibrium | Lattice parameter/pm |
|---|---|---|
| $CoSi_2$ | $CoSi_2$ | a = 536,20 |
| $Co_{0.95}Fe_{0.05}Si_2$ | | a = 536,38 |
| $Co_{0.93}Fe_{0.07}Si_2$ | | a = 536,55 |
| $Co_{0.75}Fe_{0.25}Si_2$ | $\alpha$-$FeSi_2$+MK1+MK2 | |
| $Co_{0.25}Fe_{0.75}Si_2$ | $\alpha$-$FeSi_2$+$\beta$-$FeSi_2$+MK1+MK2 | |

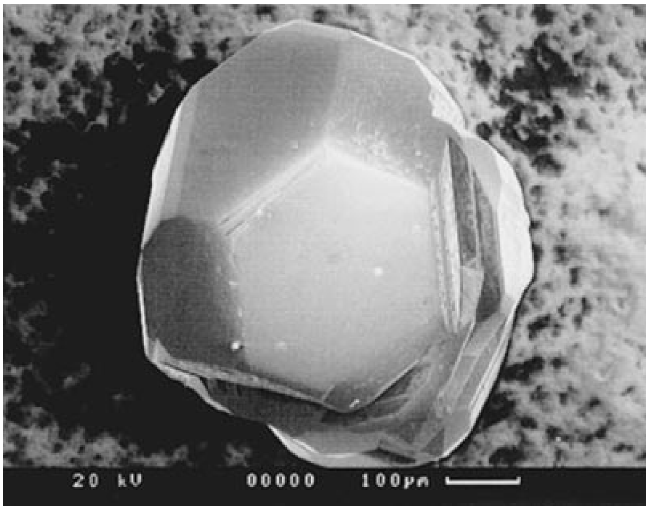

**Fig. 4** Single crystal of $Co_xFe_{1-x}Si$ obtained by chemical transport with iodine.

calculated for the cubic unit cell ($CoSi_2$). The results are given in Table 2.

The lattice constant of $CoSi_2$ increases by substitution with iron in the lattice. From the initial composition of more than 7 Mol% $\beta$-$FeSi_2$, the equilibrium state is unclear so far. Always $\alpha$-$FeSi_2$ has been found as a second phase. From the initial composition $Co_{0,75}Fe_{0,25}Si_2$ additional $Co_xFe_{1-x}Si_{1\pm y}$ (MK1) has been found, and from the initial composition $Co_{0.25}Fe_{0.75}Si_2$ additional $\beta$-$FeSi_2$ has been found (Table 2).

## 4 Chemical Vapour Transport and Characterization

Single crystals of ternary silicides should be obtainable by chemical vapour transport. Using own experiences on transport of the binary phases and results from literature [1, 2, 6−8] iodine was chosen as the transport agent. Appropriate mixtures of the elements have been used for vapour transport of disilicides, while single phase powders from the solid state reaction are used for the transport of monosilicides. Usually, after a 24 h preheating period in a reversed temperature gradient, the ampoule remains for about 10 days at the transport temperature.

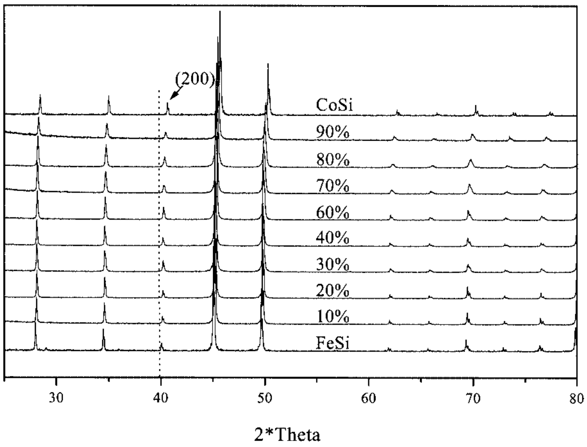

**Fig. 5** Powder diffraction patterns of ground $Co_xFe_{1-x}Si$ crystals

**Table 3** Average transport rate (TR) and composition of deposited mixed crystals

| Initial composition | $TR_{aver.}$ mg/h | ESMA | X-Ray, a/pm Depos. crystals. | Resulting composition. | ICP-OES |
|---|---|---|---|---|---|
| FeSi | 1,4 | | – | | $FeSi_{0,99}$ |
| $Co_{0,1}Fe_{0,9}Si$ | 1,6 | $Co_{0,1}Fe_{0,9}Si$ | 448,6 | $Co_{0,09}Fe_{0,91}Si$ | $Co_{0,02}Fe_{0,99}Si_{0,99}$ |
| $Co_{0,2}Fe_{0,8}Si$ | 1,5 | $Co_{0,04}Fe_{0,96}Si$ | 448,6 | $Co_{0,09}Fe_{0,91}Si$ | |
| $Co_{0,3}Fe_{0,7}Si$ | 0,6 | $Co_{0,24}Fe_{0,76}Si$ | 448,2 | $Co_{0,18}Fe_{0,82}Si$ | |
| $Co_{0,4}Fe_{0,6}Si$ | 0,9 | $Co_{0,16}Fe_{0,84}Si$ | 448,4 | $Co_{0,14}Fe_{0,86}Si$ | |
| $Co_{0,5}Fe_{0,5}Si$ | 1,3 | $Co_{0,08}Fe_{0,92}Si$ | 448,7 | $Co_{0,07}Fe_{0,93}Si$ | $Co_{0,14}Fe_{0,87}Si$ |
| $Co_{0,6}Fe_{0,4}Si$ | 0,5 | $Co_{0,42}Fe_{0,58}Si$ | 448,3 | $Co_{0,16}Fe_{0,84}Si$ | |
| $Co_{0,7}Fe_{0,3}Si$ | 0,4 | $Co_{0,28}Fe_{0,72}Si$ | 447,6 | $Co_{0,32}Fe_{0,68}Si$ | $Co_{0,27}Fe_{0,73}Si_{1,03}$ |
| $Co_{0,8}Fe_{0,2}Si$ | 0,3 | $Co_{0,54}Fe_{0,46}Si$ | 447,2 | $Co_{0,41}Fe_{0,59}Si$ | |
| $Co_{0,9}Fe_{0,1}Si$ | 0,2 | $Co_{0,84}Fe_{0,16}Si$ | 446,2 | $Co_{0,64}Fe_{0,36}Si$ | |
| CoSi | 0,2 | | – | | $CoSi_{0,94}$ |

### *4.1 The system CoSi/FeSi*

Investigations of chemical vapour transport have shown that single crystals of ternary silicides can be obtained from the gaseous phase. The transport takes place from lower to higher temperature as also observed for the binary phases. Figure 4 presents an electron micrograph of a single crystal prepared by chemical vapour transport of $Co_{0.4}Fe_{0.6}Si$. The chemical vapour transport has been performed from 973 K to 1173 K with 12 mg $I_2$ as transport agent. The aim of the transport experiments was to obtain single crystals of the solid solution series $Co_xFe_{1-x}Si$. The homogeneity range concerning the silicon content, $Co_xFe_{1-x}Si_{1\pm y}$, is not in our focus.

The average transport rates for the system Co/Fe/Si are given in Table 3. With an increasing amount of cobalt the average transport rates decrease from 1.4 mg/h to 0,2 mg/h.

The diffraction patterns of ground $Co_xFe_{1-x}Si$ single crystals demonstrate a systematic shift of the lattice parameters. Because of the substitution of iron by cobalt in the lattice of FeSi, there is a shift of the reflections to higher diffraction angles as shown in Fig. 5.

A comparison between the initial composition and the deposited composition always shows an enrichment of iron in the deposited crystals at the transport conditions described. Therefore, a lowering of the iron content take place in the starting material.

**Table 4** Thermodynamic data of mixed crystals $Co_xFe_{1\text{-}x}Si$

| Formula | $H°_{298}$ cal/mol | $\Delta_M H°$ cal/mol $\Omega = 10000$ | $S°_{298}$ cal/(mol K) | Cp° A B*$10^3$ C*$10^{-5}$ cal/(mol K) | $\Delta_M S°$ cal/(mol K) |
|---|---|---|---|---|---|
| FeSi | −18500 | 0 | 11 | 10,63/ 3,537/0 | 0 |
| $Fe_{09}Co_{01}Si$ | −18951 | −900 | 11,576 | 10,74/3,472 | −0,644 |
| $Fe_{08}Co_{02}Si$ | −19402 | −1600 | 11,856 | 10,85/3,408 | −0,992 |
| $Fe_{07}Co_{03}Si$ | −19853 | −2100 | 12,008 | 10,96/3,343 | −1,212 |
| $Fe_{06}Co_{04}Si$ | −20304 | −2400 | 12,063 | 11,07/3,278 | −1,335 |
| $Fe_{05}Co_{05}Si$ | −20755 | −2500 | 12,035 | 11,19/3,214 | −1,375 |
| $Fe_{04}Co_{06}Si$ | −21206 | −2400 | 11,927 | 11,30/3,149 | −1,335 |
| $Fe_{03}Co_{07}Si$ | −21657 | −2100 | 11,736 | 11,41/3,084 | −1,212 |
| $Fe_{02}Co_{08}Si$ | −22108 | −1600 | 11,448 | 11,52/3,019 | −0,992 |
| $Fe_{01}Co_{09}Si$ | −22559 | −900 | 11,032 | 11,63/2,955 | −0,644 |
| CoSi | −23010 | 0 | 10,32 | 11,74/ 2,89/ 0 | 0 |

To describe the substitution of cobalt in the lattice of FeSi exactly, the X-ray diffraction diagrams have been refined by the Rietveld method and the lattice constants were obtained from that procedure. The results are given in Table 3 and Figure 6b. The course of iron enrichment in dependence on the initial composition is recognizable. EDX analysis and ICP-OES have been used to confirm these results, and the EDX analysis confirm the results obtained by X-ray except for some deviations which are difficult to declare. The X-ray and EDX results are based on the compounds $Co_xFe_{1\text{-}x}Si$.

From selected transport experiments five monocrystals were dissolved in HF and analysed with ICP-OES (Table 3). The results agree well with data obtained with other methods, but further investigations are necessary. The ICP-OES allows a precise measurement of the silicon content. The results confirm the homogeneity range assumed by us.

### *4.1.1 Calculations of the transport behaviour in the system CoSi-FeSi*

The shift in the Co/Fe ratio observed by deposition from the gas phase should be confirmable by model calculations. The reason for this is a incongruently solution of compounds in the gas phase.

The program TRAGMIN [9] has been used for calculations. To describe the transport of the silicides for the calculation we have used thermodynamic data of gaseous species which are given in [1, 2]. To estimate data for the mixed crystals $Co_xFe_{1\text{-}x}Si$, we used a regular solution with a regularity parameter $\Omega = -10$ kcal/mol. Calculations with a ideal solution (regularity parameter $\Omega = 0$ kcal/mol) have given much worse results. For the calculation the binary phases FeSi and CoSi are considered as pseudo components and an arbitrary amount of quasistoichiometric phases $Co_xFe_{1\text{-}x}Si$ has been formulated. The program calculates the equilibrium between the gas phase and one or two “stoichiometric” phases depending on the initial composition. The deposited composition will be calculated with respect of the transport conditions, for example the temperature gradient, compare with [12].

Using the equations (1)-(7), thermodynamic data of the $Co_xFe_{1\text{-}x}Si$ compounds could be obtained. Tabel 4 shows the data used for calculations.

$$G°(Co_xFe_{1\text{-}x}Si) = xG°(CoSi) + (1\text{-}x)G°(FeSi) + \Delta_M G° \tag{1}$$

$$H°(Co_xFe_{1\text{-}x}Si) = xH°(CoSi) + (1\text{-}x)H°(FeSi) + \Delta_M H° \tag{2}$$

$$S°(Co_xFe_{1\text{-}x}Si) = xS°(CoSi) + (1\text{-}x)S°(FeSi) + \Delta_M S° \tag{3}$$

$$Cp°(Co_xFe_{1\text{-}x}Si) = A + B10^{-3}T + C10^5T^{-2} \tag{4}$$

$$A(Co_xFe_{1\text{-}x}Si) = xA(CoSi) + (1\text{-}x)A(FeSi) \tag{5}$$

$$\Delta_M S° = xR\ln x + (1\text{-}x)R\ln(1\text{-}x) \tag{6}$$

$$\Delta_M H° = \Omega x(1\text{-}x) \tag{7}$$

The results of the calculations are shown in Figure 6a. The initial compositions are given on top and the deposited on bottom of the x-axis. Starting from an initial composition of $Co_{0.6}Fe_{0.4}Si$ a deposit of $Co_{0.4}Fe_{0.6}Si$ has been calculated at the given conditions. Figure 6b shows the experimental results analysed by EDX and X-ray for comparison.

The results show the possibility to calculate the shift of the composition of chemical transport reactions. The comparison of absolute values is not satisfying due to the deviation of the individual values.

### *4.1.2 Measurements of the electrical properties in the system CoSi/FeSi*

First resistivity investigations on single crystals are shown in Figure 7. CoSi shows metallic behaviour whereas FeSi is comparable with a semiconductor. This results agree well with literature data [6, 10]. The resistivity of our FeSi crystals is two orders of magnitude higher than the values *Kloc* et al. [6] have been observed. The resistivity of the mixed crystals decreases with increasing cobalt content, see Figure 7a. Due to the irregularities and the small size of the crystals errors at the measurements are likely. Figure 7b shows the temperature dependence on the resistivity of FeSi. From the $\ln\rho = f(1/T)$ plot we got the activation energy of the

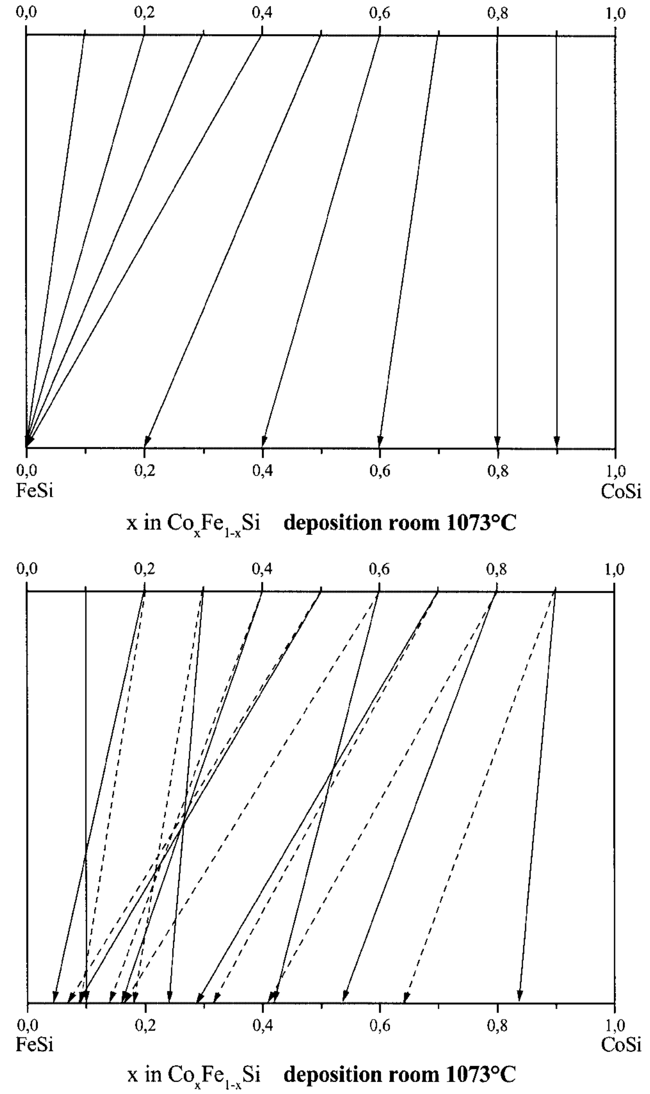

**Fig. 6** (top) Calculated transport behaviour in the system $Co_xFe_{1-x}Si$; (bottom) Experimental results of transport in the system $Co_xFe_{1-x}Si$ analysed by EDX (full line) and X-ray (dashed line)

conductivity. A value of 19.5 meV was calculated below 160 K. This value is smaller than those given in [6]. Further investigations are necessary to explain the deviations.

## *4.2 The system $CoSi_2$/β-$FeSi_2$*

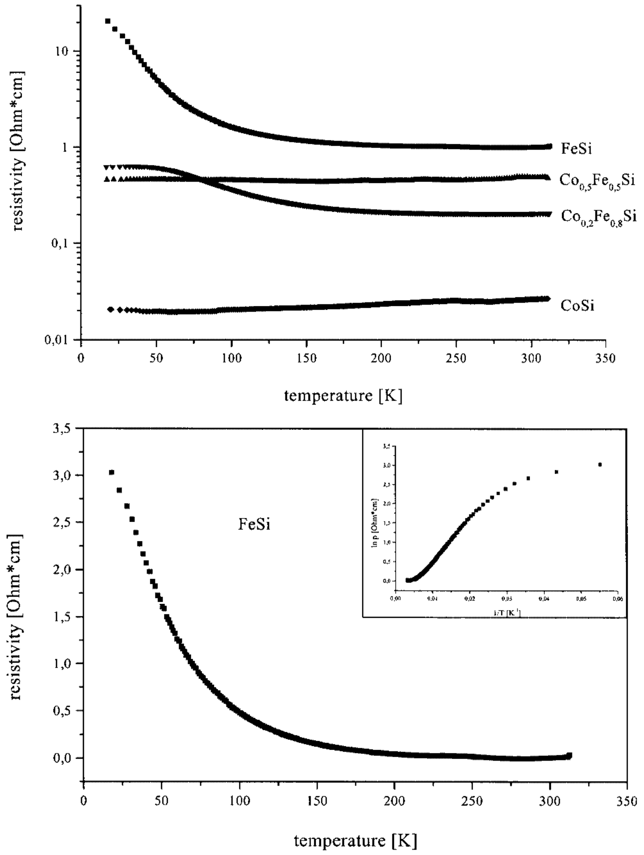

**Fig. 7** (top) Resistivity of $Co_xFe_{1-x}Si$ crystals; (bottom) Resistivity of FeSi crystals

Only few transport experiments have been undertaken in this system. The transport direction from higher temperature to lower temperature for disilicides is known from own transport experiments on the binary phases [1, 2] and from our calculations, too. For the chemical transport reactions mixtures of iron, cobalt and silicon have been used. The initial compositions were $Co_{0.05}Fe_{0.95}Si_2$, $Co_{0.25}Fe_{0.75}Si_2$, $Co_{0.75}Fe_{0.25}Si_2$, $Co_{0.95}Fe_{0.05}Si_2$. With notes from the literature [6, 7] describing the transport of β-$FeSi_2$, we used a temperature gradient from 1323 K (solution room) to 1123 K and 100 mg iodine as transport agent. On the iron rich side of the system we observed chemical transport up to $Co_{0.25}Fe_{0.75}Si_2$. First a transport of silicon has been observed. The second step of the transport is the deposition of $Co_xFe_{1-x}Si_{1\pm y}$ (MK1), found on the surface of the silicon crystals [Figure 8b].

In addition needle like single crystals of β-$FeSi_2$ were deposited in the middle of the ampoules (Figure 8 c and d) with dimensions of (4 to 9) x 2 x 0.5 mm³. These β-$FeSi_2$ crystals have been checked by X-ray and EDX, no cobalt content and no shift of d-spacing have been observed. A logical conclusion of the coexistence of β-$FeSi_2$ and $Co_xFe_{1-x}Si_{1\pm y}$ (MK1) is that the composition of $Co_xFe_{1-x}Si_{1\pm y}$ (MK1) is the upper phase boundary of $Co_xFe_{1-x}Si_{1+y}$. The residue after 14 days of chemical vapour transport was $Co_xFe_{1-x}Si_{1\pm y}$ (MK1).

On the cobalt rich side of the system first deposits were obtained only after 10 days. The few single crystals obtained, were identified by X-ray as α-$FeSi_2$ (Figure 8 a), $Co_xFe_{1-x}Si_{1\pm y}$ (Figure 8 b ), Si and $Fe_3Si$. The observation of up to four phases simultaneously indicates a non-equilibrium state.

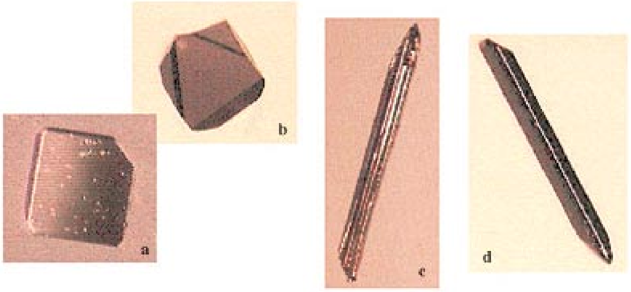

**Fig. 8** Single crystals grown by chemical vapor transport of a) α-$FeSi_2$, b) $Co_xFe_{1-x}Si_{1\pm y}$, c) and d) β-$FeSi_2$.

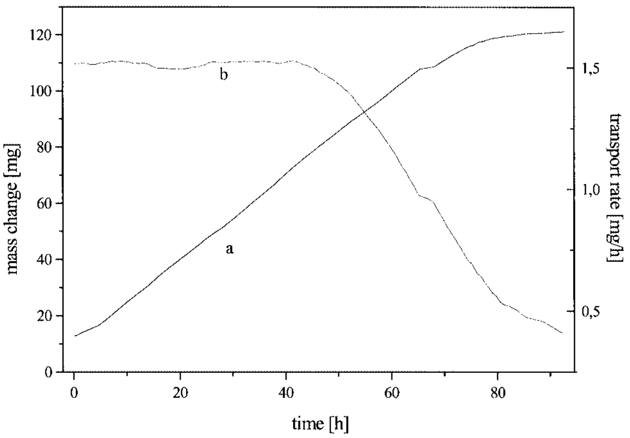

**Fig. 9** Chemical vapour transport of FeSi (973 K to 1073 K)

## 5 Transport Balance

For continuous studies of transport processes a so called transport balance was built up.

Our equipment is comparable with that described in the literature [11]. The stored data (weight change per time interval) can be smoothed mathematically and represented graphically. The transport rates are obtained by differentiation of measured data. The functionality of the method is demonstrated by two examples.

It was possible to show that the chemical vapour transport of FeSi could be described as a steady state transport, see Figure 9. The transport rates calculated could be confirmed.

Figure 9 shows a representative course of weight change (a) because of the deposition of FeSi in the sink. Graph b indicates the incident transport rate as function of time. As expected, the transport rate is nearly constant at 1.6 mg/h. At the end of the experiment the transport rate drops to zero because of the consumption of the source material.

Figure 10 shows the time course of transport rates of the chemical vapour transport of β-$FeSi_2$. The transport conditions are the same as given in part 4.2. Graph a shows again the course of weight change, whereas graph b displays transport rates. In this graph two stages with different slope are presented. From previous, tentative experiments we assume that several steady states appear depending on the composition of source and sink, respectively.

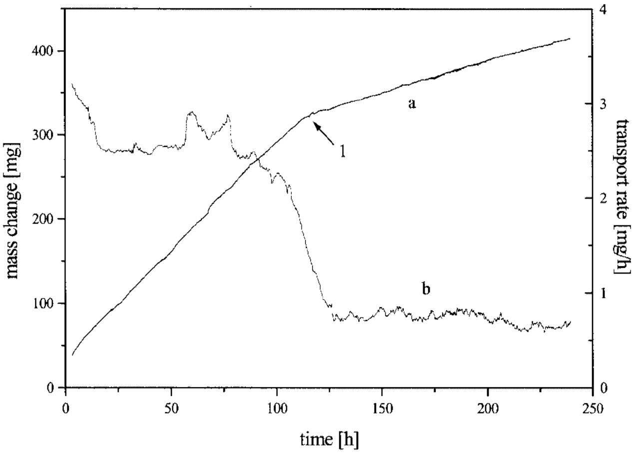

**Fig. 10** Chemical vapour transport of β-$FeSi_2$ (1273 K to 1073 K, agent: 100 mg iodine)

Earlier experiments have shown that FeSi, β-$FeSi_2$, and α-$FeSi_2$ in the source exist after 4 days of transport. From such a source mainly silicon and FeSi are deposited at the beginning of the experiments, see Figure 10 up to point 1. Later the deposition of FeSi and β-$FeSi_2$ is observed with a smaller transport rate. At the end of the transport experiment the deposit of FeSi besides and on the surface of silicon is situated at the colder end of the ampoule. In the middle of the ampoule we found a needle-like deposit of β-$FeSi_2$. The description of the transport behaviour of β-$FeSi_2$ shows some unclearness. Therefore, further investigations are necessary.

*Acknowledgment.* The authors wish to thank *Dr. M. Dörr* (TUD, Institut für Angewandte Physik und Didaktik der Physik) for electrical measurements, *Priv.-Doz. Dr. S. Däbritz* and *E. Langer* (TUD, Institut für Oberflächen- und Mikrostrukturphysik) for EDX investigations, Mrs. *U. Schmidt* (MPI CPfS, Dresden) for ICP-OES investigations, *Prof. Dr. R. Glaum* (Universität Bonn) and *Dr. G. Behr* (IFW Dresden) for the support of building up the transport balance. Financial support of the Deutsche Forschungsgemeinschaft (Projekt Op 62/5-4) is gratefully acknowledged.

## References

[1] O. Bosholm, H. Oppermann, S. Däbritz, *Z. Naturforsch.* **2000**, *55b*, 614.

[2] O. Bosholm, H. Oppermann, *Z. Naturforsch.* **2000**, *55b*, 1199.

[3] A. Wittmann, K. O. Burger, H. Nowotny, *Monatsh. Chem.* **1962**, *93*, 774.

[4] H. Massalski, *Binary Alloy Phase Diagrams*, Second Edition, ASM International 1996.

[5] A. Wittmann, K. O. Burger, H. Nowotny, *Monatsh. Chem.* **1961**, *92*, 64.

[6] Ch. Kloc, E. Arushanov, M. Wendl, H. Hohl, U. Malang, E. Bucher, *J. Alloys Compds.* **1995**, *219*, 93.

[7] G. Behr, J. Werner, G. Weise, A. Heinrich, A. Burkov, C. Gladun, *Phys. Stat. Sol. (a)***1997**, *160*, 549.

[8] R. Wandij, Y. Dusausoy, J. Portas, B. Roques, *C. R. Acad. Sci. Paris* **1968**, *C 267*, 1587.

[9] G. Krabbes, W. Bieger, K.-H. Sommer, T. Söhnel, *Programmpaket TRAGMIN,* IFW Dresden, TU Dresden, Institut für Anorganische Chemie.

[10] J. Prokop, C. E. Zybill, S. Veprek, *Thin Solid Films* **2000**, *359*, 39.

[11] V. Plies, T. Kohlmann, R. Gruehn, *Z. Anorg. Allg. Chem.* **1989**, *568*, 62; R. Gruehn, R. Glaum, *Angew. Chem.* **2000**, *112*, 706; *Angew. Chem. Int. Ed.* **2000**, *39*, 692.

[12] W. Reichelt, U. Steiner, *Proc. ECSSC-8*, Oslo, 2001.