Quaternary rare earth transition metal arsenide oxides *RT*AsO (*T*=Fe, Ru, Co) with ZrCuSiAs type structure

P. Quebe, L.J. Terbüchte, W. Jeitschko*

Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Straße 8, D-48149 Münster, Germany

Abstract

The equiatomic quaternary compounds *R*FeAsO (*R*=La–Nd, Sm, Gd), *R*RuAsO (*R*=La–Nd, Sm, Gd–Dy) and *R*CoAsO (*R*=La–Nd) crystallize with the tetragonal ZrCuSiAs type structure, which was refined from single-crystal X-ray diffractometer data of PrFeAsO: $P4/nmm$, $Z=2$, $a=398.5(1)$ pm, $c=859.5(3)$ pm, $R=0.058$ for 167 structure factors and 12 variable parameters. All atomic positions are fully occupied. Chemical bonding in PrFeAsO can be rationalized with oxidation numbers corresponding to the formula $Pr^{+3}Fe^{+2}As^{-3}O^{-2}$. An electron count of 18 for the iron atoms can only be achieved if Fe–Fe interactions of 281.8 pm are considered as bonding. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rare earth compounds; Arsenide oxides; Single crystal X-ray diffraction; Structure determination

1. Introduction

The quaternary equiatomic ZrCuSiAs type structure is very simple with only eight atoms in the tetragonal cell. It was first described as a 'filled' PbFCl type structure [1]. Oxygen containing compounds with this structure were reported in combination with sulfur, selenium and tellurium as the other anionic component, e.g. the solid electrolyte LaAgSO [2,3] with silver ions as conducting species, the corresponding copper compound LaCuSO [4,5], the series *R*CuSeO (*R*=Y, La, Sm, Gd [6] and *R*=Nd, Gd, Dy, Bi [7,8]), BiCuSO [7], *R*CuSO (*R*=Nd, Sm) [9] and LaCuTeO [9]. With oxygen and the pnictogens as anionic components the following compounds were reported: UCuPO [10], *R*FePO (*R*=La–Nd, Sm, Gd) [11], *R*RuPO (*R*=La–Nd, Sm, Gd) [11], *R*CoPO (*R*=La–Nd, Sm) [11], ThCuPO [12], ThCuAsO [12], *R*ZnSbO (*R*=La–Nd, Sm) [13], *R*MnPO (*R*=La–Nd, Sm, Gd–Dy) [14], *R*MnAsO (*R*=Y, La–Nd, Sm, Gd–Dy, U) [14], *R*MnSbO (*R*=La–Nd, Sm, Gd) [14], *R*ZnPO (*R*=La, Ce) [15] and *R*ZnAsO (*R*=Y, La–Nd, Sm, Gd–Tm) [15]. Furthermore, the sulfide and selenide fluorides BaCuSF and BaCuSeF are known [16].

In addition to quaternary compounds with ZrCuSiAs type structure ternary compounds with this symmetry and identical atomic positions are known, where the silicon and the arsenic positions of ZrCuSiAs are occupied by the same atomic species, e.g. the silicides and germanides $ZrCuSi_2$ and $HfCuSi_2$ [17,18], $ZrCuGe_2$ and $HfCuGe_2$ [18], the uranium compounds $UTPn_2$ (*T*=Fe, Co, Ni, Cu; *Pn*=P, As, Sb, Bi) [19,20], the calcium bismuth compound $CaMnBi_2$ [21], the lanthanum transition metal antimonides $LaT_{1-x}Sb_2$ (*T*=Mn, Co, Cu, Zn, Cd) with considerable defects for the *T* sites [22–24] and various series of additional rare earth transition metal antimonides where the defects for the *T* sites frequently have not been investigated: $RMnSb_2$ [23,24], $RFeSb_2$ [25], $RCoSb_2$ [24,25], $RNiSb_2$ [26,27], $RPdSb_2$ [27], $RCuSb_2$ [27], $RAgSb_2$ [28,29], $RAuSb_2$ [24,27], $RZnSb_2$ [23,24] and $RCdSb_2$ [23,24]. With arsenic only the copper series $RCuAs_2$ [28] is known and it seems that a large number of bismuthides could be prepared, since the cerium compounds $CeTBi_2$ (*T*=Ni, Cu, Ag, Zn) have been reported [30]. All together more than 200 representatives with this structure have been characterized. Among the more interesting properties of such compounds mixed or intermediate valence can be expected for compounds containing cerium, europium, ytterbium or uranium [30–32] as well as interesting thermal and electrical transport properties of the

*Corresponding author. Tel.: +49-251-833-3121; fax: +49-251-833-3136.

more metallic compositions [31,32]. Here we report the new quaternary series of rare earth transition metal arsenide oxides RFeAsO, RRuAsO and RCoAsO.

2. Sample preparation and lattice constants

Most of the quaternary compounds reported here were obtained first as byproducts of ternary samples without intentional addition of oxygen. Subsequently many of these compounds were prepared from quaternary samples, where the oxygen was introduced by powders of the transition metal oxides: Fe_2O_3 (Riedel–de Haën, "rein"), RuO_2 (Ventron, 99.9%) and Co_3O_4 (Merck, "rein"). It is not advisable to use oxides of the rare earth elements as a source for oxygen since, because of their high stability, they do not readily react with the other components of the mixture. The rare earth elements were purchased in the form of ingots with nominal purity 99.9%. Filings of these were prepared under dry (Na) paraffin oil, which was removed by dry n-hexane. The transition metals were purchased as powders with nominal purities of 99.5% (Fe, Co) and 99.9% (Ru). The arsenic pieces (>99%) were purified by fractional crystallization. First the arsenic oxide (As_2O_3) is sublimated under vacuum at 350°C, then the elemental arsenic at 550°C.

The iron containing compounds were obtained from samples with the atomic ratio R:Fe:Fe_2O_3:As=3:1:1:3. These powders (300 mg) were added to a NaCl/KCl mixture (1:1, 2 g), sealed into evacuated silica tubes and annealed for 2 weeks at 800°C. It should be emphasized that the NaCl/KCl flux only dissolves minor amounts of the metallic components. Hence, it may be regarded as a mineralizer, which enhances the formation of the quaternary compounds. After the annealing, the NaCl/KCl matrix was dissolved in water at room temperature.

For the synthesis of the compounds containing ruthenium or cobalt we prepared first the rare earth arsenides RAs by reaction of the elemental components in evacuated sealed silica tubes. The samples were placed in the hot furnace which was closed thereafter. Thus, the expected exothermic reaction was not observed. After annealing for 2 days at 500°C the reaction products were stored under argon or used immediately thereafter to prepare the quaternary compounds. These were obtained by solid state reaction of cold pressed-pellets of the ideal compositions RAs:Ru:RuO_2 and RAs:Co:Co_3O_4 in the atomic ratios 2:1:1 and 4:1:1, respectively. The annealing in evacuated silica tubes was for 1 week at 950°C. After grinding the products to a fine powder and cold-pressing, the samples were annealed again at 950°C for 2 weeks.

The quaternary compounds are stable in air for long periods of time. They are black with metallic lustre. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium. In previous investigations

Table 1
Lattice constants of the tetragonal compounds $R T$AsO[a]

Compound	a (pm)	c (pm)	c/a	V (nm^3)
LaFeAsO	403.8(1)	875.3(6)	2.168	0.1427
CeFeAsO	400.0(1)	865.5(1)	2.164	0.1385
PrFeAsO	398.5(1)	859.5(3)	2.157	0.1365
NdFeAsO	396.5(1)	857.5(2)	2.163	0.1348
SmFeAsO	394.0(1)	849.6(3)	2.156	0.1319
GdFeAsO	391.5(1)	843.5(4)	2.155	0.1293
LaRuAsO	411.9(1)	848.8(1)	2.061	0.1440
CeRuAsO	409.6(1)	838.0(3)	2.046	0.1406
PrRuAsO	408.5(1)	833.7(1)	2.041	0.1391
NdRuAsO	407.9(1)	829.2(2)	2.033	0.1380
SmRuAsO	405.0(2)	819.1(7)	2.022	0.1343
GdRuAsO	403.9(1)	811.8(6)	2.010	0.1324
TbRuAsO	402.7(1)	807.8(1)	2.006	0,1310
DyRuAsO	402.2(2)	805.0(3)	2.001	0.1302
LaCoAsO	405.4(1)	847.2(3)	2.090	0.1392
CeCoAsO	401.5(1)	836.4(2)	2.083	0.1348
PrCoAsO	400.5(1)	834.4(2)	2.083	0.1338
NdCoAsO	398.2(1)	831.7(4)	2.089	0.1319

[a] Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

of the isotypic phosphorous compounds $R T$PO (T=Fe, Ru, Co) the oxygen content of the samples had been proven by a windowless detector [11].

The samples were characterized by Guinier powder diagrams using monochromatized Cu $K\alpha_1$ radiation with α-quartz (a=491.30 pm, c=540.46 pm) as an internal standard. The lattice constants (Table 1) were obtained by least-squares fits.

3. Structure refinement of PrFeAsO

A small single-crystal (67×44×7 μm^3), isolated from the polycrystalline sample prepared with the NaCl/KCl flux, was used for the X-ray data collection on a four-circle diffractometer (CAD4) using graphite monochromatized Mo $K\alpha$ radiation and a scintillation counter with pulse-height discrimination. The scans were along the diffraction streaks up to 2θ=70° with background counts at both ends of each scan and scan velocities optimized by fast pre-scans. An absorption correction was applied from psi-scan data. A total of 1145 reflections was measured in one half of the reciprocal sphere, which resulted in 214 unique reflections (internal residual on intensity values: R_i= 0.123). The lattice constants obtained on the four-circle diffractometer (a=397.9(1) pm, c=858.0(2) pm) are slightly smaller than those from the Guinier powder data (Table 1), since they are affected by systematic errors due to absorption.

The isotypy of the structure with that of tetragonal ZrCuSiAs [1] was recognized from previous investigations [10–15]. The high Laue symmetry had been confirmed prior to the data averaging and the positional parameters of PrFePO [11] were used as starting atomic parameters for

Table 2
Atomic parameters of PrFeAsO[a]

Atom	$P4/nmm$	Occupancy	x	y	z	$B_{11}=B_{22}$	B_{33}	B_{eq}
Pr	$2c$	101.2(5)	1/4	1/4	0.1399(2)	0.03(4)	0.71(5)	0.26(4)
Fe	$2b$	98(1)	3/4	1/4	1/2	0.13(8)	0.86(11)	0.38(6)
As	$2c$	100.4(9)	1/4	1/4	0.6565(3)	0.31(6)	0.68(10)	0.44(4)
O	$2a$	96(5)	3/4	1/4	0	1.1(6)	0.4(6)	0.9(4)

[a] The occupancy parameters were obtained in a separate series of least-square cycles. In the final cycles the occupancy parameters were assumed to be ideal. The anisotropic displacement parameters are of the form $\exp[-0.25(h^2a*^2B_{11}+\cdots)]$. For symmetry reasons the values B_{12}, B_{13} and B_{23} are all equal to zero. The last column contains the equivalent isotropic displacement parameters B_{eq} ($\times 10^{-4}$, in units of pm^2).

Table 3
Interatomic distances in PrFeAsO[a]

Pr:	4 O	232.7	Fe:	4 As	240.4	As:	4 Fe	240.4	O:	4 Pr	232.4
	4 As	331.7		4 Fe	281.8		4 Pr	331.7		4 O	281.8
	4 Fe	368.1		4 Pr	368.1		4 O	356.2		4 As	356.2
	4 Pr	370.5									

[a] All distances shorter than 380 pm are listed. The standard deviations are all 0.2 pm or less.

the structure refinement with a full-matrix least-squares program [33] using atomic scattering factors, corrected for anomalous dispersion, as provided by the program. The weighting scheme accounted for the counting statistics, and a parameter correcting for isotropic secondary extinction was optimized as a least-squares variable. There are $Z=2$ formula units in the cell of space group $P4/nmm$ (No. 129), and the calculated density is 7.03 g·cm^{-3}.

To check the composition we refined occupancy values in one series of least-squares cycles together with anisotropic displacement parameters and a fixed scale factor. The results are shown in the third column of Table 2. It can be seen that all atoms have the ideal occupancy values within three standard deviations. Therefore in the final least-squares cycles we resumed to the ideal occupancy values. A conventional residual of $R=0.058$ was obtained

for 167 structure factors greater than 2σ. The weighted residual was 0.146 for 214 F^2 values and 12 variable parameters. The highest residual electron densities in the final difference Fourier synthesis of 9.7 and 4.0 e Å^{-3} were too close to the fully occupied Pr (61 pm) and As (37 pm) positions to be suited for additional atomic sites. The final atomic parameters and interatomic distances are listed in Tables 2 and 3.

4. Discussion

The new ZrCuSiAs type compounds RFeAsO, RRuAsO and RCoAsO are represented by their cell volumes in Fig. 1 together with the cell volumes of isotypic compounds with related compositions reported earlier [11]. In general,
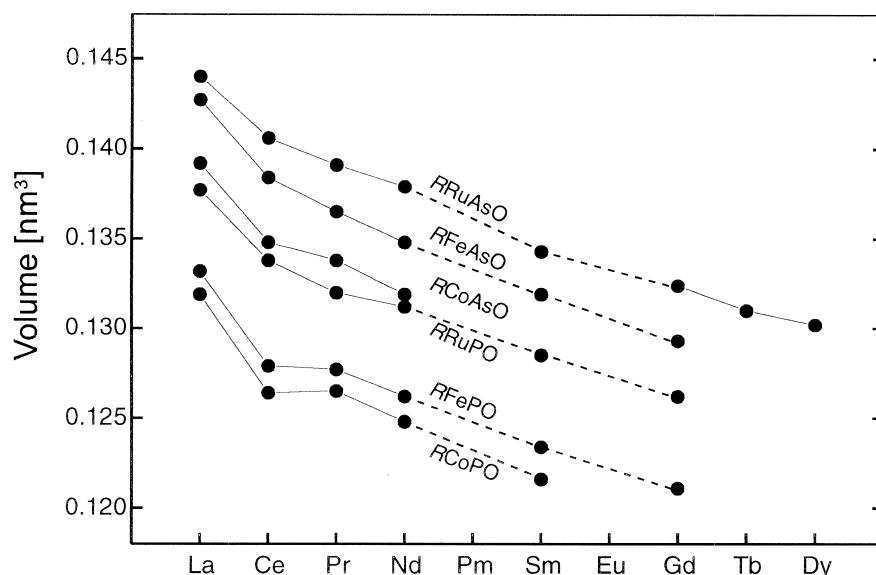

Fig. 1. Cell volumes of compounds $RTPn$O (T=Fe, Ru, Co; Pn=P, As) with ZrCuSiAs type structure.

the cell volumes of the new arsenide oxides follow the well known lanthanoid contraction of the trivalent rare earth elements. For the series of arsenide oxides a slight deviation from the smooth decrease, almost within the error limits, occurs for CeCoAsO, which may be rationalized by an intermediate or mixed valence of cerium ($Ce^{+3/+4}$). In the series of compounds containing phosphorus, larger deviations occur for CeFePO and CeCoPO indicating a larger proportion of Ce^{+4}. This may be rationalized by the higher electronegativity of phosphorus as compared to arsenic. The fact that CeRuPO fits rather well into the plot of the compounds of the corresponding trivalent rare earth elements seems to be an exception. However, similar ''exceptions'' were observed for the cell volumes of the polyphosphides and polyarsenides RT_4P_{12} and RT_4As_{12}, where the deviations are large for T=Fe and small for T=Ru and Os [34]. The fact that the lanthanum compounds are formed for all of the investigated series RTPO and RTAsO suggests that it might be possible to prepare one or the other corresponding strontium or barium compound.

In contrast, with the smaller rare earth elements, we have been successful to prepare only TbRuAsO and DyRuAsO. The corresponding compounds RFeAsO, briefly mentioned as ternary 'TbFeAs' and 'DyFeAs' at a conference [35], have not yet been reproduced as quaternary arsenide oxides. These compounds were obtained as byproducts in small amounts and we have not reproduced these results with the intentional addition of oxygen. In all cases where the oxygen has been added intentionally in the form of the binary transition metal oxides Fe_2O_3, RuO_2 and Co_3O_4 there was excellent agreement (within four combined standard deviations) between the lattice constants of the ''ternary'' and quaternary samples. For that reason we believe that the ZrCuSiAs (''filled'' PbFCl) type compounds found in ''ternary'' samples were stabilized by oxygen and not by nitrogen, although it seems possible that the corresponding nitrides also could be prepared. Since the scattering power of these light elements is small, the observed Guinier powder patterns of these quaternary compounds agree well with patterns calculated, assuming both the filled or unfilled PbFCl type structure.

Chemical bonding in the quaternary pnictide oxides can be rationalized by simple models using PrFeAsO as an example. Since the praseodymium atoms are relatively far apart from each other (Table 3) we exclude any substantial Pr–Pr bonding and we count the valence electrons of the praseodymium atoms at the more electronegative arsenic and oxygen atoms. In analogy, there are no short As–As, As–O or O–O interactions and therefore, in agreement with the octet rule, we arrive at the oxidation numbers -3 and -2 for the arsenic and oxygen atoms, respectively. This does not contradict more or less covalent Fe–As or Fe–O interactions. The corresponding bonding electrons are only *counted* at the arsenic and oxygen atoms. The important result of this rationalization lies in the fact that

the iron atoms obtain the oxidation number $+2$, according to the formula $Pr^{+3}Fe^{+2}As^{-3}O^{-2}$. Thus, each iron atom possesses six electrons (a ''d^6-system'') which are not involved in interactions with the atoms of the other elements.

Each arsenic atom has four iron neighbours, and since we assume its octet to be filled, we could count two electrons for each of the four As–Fe interactions. However, if we look at the coordination of the arsenic atoms (Fig. 2) we see that the four iron neighbours of an arsenic atom are all at one side; at the opposite side the arsenic atom is coordinated by praseodymium atoms. Thus, a count of two electrons for each As–Fe interaction is at best an upper limit. Conversely, we can also count these bonding electrons at the iron atoms: at most two for each of the four tetrahedral Fe–As bonds. Hence, we may obtain an electron count of 14 for each iron atom: (at most) 8 electrons from the 4 Fe–As interactions plus 6 electrons of the d^6-system. We note that each iron has, in addition to the 4 strongly bonded arsenic atoms, 4 iron neighbours in square-planar arrangement with the rather long Fe–Fe distance of 281.8 pm. Nevertheless, we can assume some Fe–Fe bonding. The electrons needed for these interactions come from the d^6-system. Since the electrons of these bonding Fe–Fe interactions are now counting at both iron atoms of an Fe–Fe bond, the total electron count for each
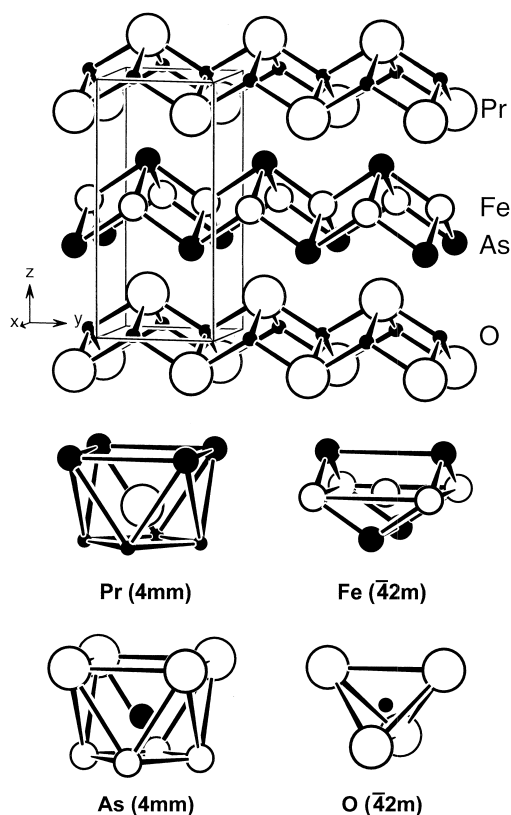

Fig. 2. Crystal structure and near-neighbour coordinations of the tetragonal ZrCuSiAs type compound PrFeAsO. The site symmetries of the central atoms of the coordination polyhedra are indicated in parentheses.

iron atom is greater than 14, possibly as high as 18, the inert gas shell.

References

[1] V. Johnson, W. Jeitschko, J. Solid State Chem. 11 (1974) 161.
[2] M. Palazzi, C. Carcaly, J. Flahaut, J. Solid State Chem. 35 (1980) 150.
[3] M. Palazzi, S. Jaulmes, Acta Crystallogr. B37 (1981) 1337.
[4] M. Palazzi, C.R. Acad. Sci. Paris 292 (1981) 789.
[5] Y. Takano, C. Ogawa, Y. Miyahara, H. Ozaki, K. Sekizawa, J. Alloys Comp. 249 (1997) 221.
[6] W.J. Zhu, Y.Z. Huang, C. Dong, Z.X. Zhao, Mater. Res. Bull. 29 (1994) 143.
[7] A.M. Kusainova, P.S. Berdonosov, L.G. Aksel'rud, L.N. Kholodkovskaya, V.A. Dolgikh, B.A. Popovkin, J. Solid State Chem. 112 (1994) 189.
[8] P.S. Berdonosov, A.M. Kusainova, L.N. Kholodkovskaya, V.A. Dolgikh, L.G. Aksel'rud, B.A. Popovkin, J. Solid State Chem. 118 (1995) 74.
[9] B.A. Popovkin, A.M. Kusainova, V.A. Dolgikh, L.G. Aksel'rud, Russian J. Inorg. Chem. 43 (1998) 1471.
[10] D. Kaczorowski, J.H. Albering, H. Noël, W. Jeitschko, J. Alloys Comp. 216 (1994) 117.
[11] B.I. Zimmer, W. Jeitschko, J.H. Albering, R. Glaum, M. Reehuis, J. Alloys Comp. 229 (1995) 238.
[12] J.H. Albering, W. Jeitschko, Z. Naturforsch. 51b (1996) 257.
[13] P. Wollesen, J.W. Kaiser, W. Jeitschko, Z. Naturforsch. 52b (1997) 1467.
[14] A.T. Nientiedt, W. Jeitschko, P.G. Pollmeier, M. Brylak, Z. Naturforsch. 52b (1997) 560.
[15] A.T. Nientiedt, W. Jeitschko, Inorg. Chem. 37 (1998) 386.
[16] W.J. Zhu, Y.Z. Huang, F. Wu, C. Dong, H. Chen, Z.X. Zhao, Mater. Res. Bull. 29 (1994) 505.
[17] H. Sprenger, J. Less-Common Met. 34 (1974) 39.
[18] L.S. Andrukhiv, L.A. Lysenko, Ya.P. Yarmolyuk, E.I. Gladyshevskii, Dopov. Akad. Nauk Ukr. RSR, Ser. A (1975) 645.
[19] J. Stępień-Damm, D. Kaczorowski, R. Troć, J. Less-Common Met. 132 (1987) 15.
[20] D. Kaczorowski, J. Alloys Comp. 186 (1992) 333.
[21] E. Brechtel, G. Cordier, H. Schäfer, Z. Naturforsch. 35b (1980) 1.
[22] G. Cordier, H. Schäfer, P. Woll, Z. Naturforsch. 40b (1985) 1097.
[23] O. Sologub, K. Hiebl, P. Rogl, O.I. Bodak, J. Alloys Comp. 227 (1995) 40.
[24] P. Wollesen, W. Jeitschko, M. Brylak, L. Dietrich, J. Alloys Comp. 245 (1996) L5.
[25] A. Leithe-Jasper, P. Rogl, J. Alloys Comp. 203 (1994) 133.
[26] Yu.V. Pankevich, V.K. Pecharskii, O.I. Bodak, Izv. Akad. Nauk SSSR, Met. (1983) 227.
[27] O. Sologub, K. Hiebl, P. Rogl, H. Noël, O.I. Bodak, J. Alloys Comp. 210 (1994) 153.
[28] M. Brylak, M.H. Möller, W. Jeitschko, J. Solid State Chem. 115 (1995) 305.
[29] O. Sologub, H. Noël, A. Leithe-Jasper, P. Rogl, O.I. Bodak, J. Solid State Chem. 115 (1995) 441.
[30] H. Flandorfer, O. Sologub, C. Godart, K. Hiebl, A. Leithe-Jasper, P. Rogl, H. Noël, Solid State Commun. 97 (1996) 561.
[31] Y. Muro, N. Takeda, M. Ishikawa, J. Alloys Comp. 257 (1997) 23.
[32] K.D. Myers, S.L. Bud'ko, I.R. Fisher, Z. Islam, H. Kleinke, A.H. Lacerda, P.C. Canfield, J. Magn. Magn. Mater. 205 (1999) 27.
[33] G.M. Sheldrick, SHELX-97, a Program Package for the Solution and Refinement of Crystal Structures, Universität Göttingen, Germany, 1997.
[34] Ch.B.H. Evers, W. Jeitschko, L. Boonk, D.J. Braun, Th. Ebel, U.D. Scholz, J. Alloys Comp. 224 (1995) 184.
[35] L.J. Terbüchte, W. Jeitschko, Z. Kristallogr. 186 (1989) 291.