ZrCuSiAs-type Phosphide Oxides: TbRuPO, DyRuPO, the Series *Ln*OsPO (*Ln* = La, Ce, Pr, Nd, Sm), and ThAgPO

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The title compounds were prepared by solid-state reactions and *via* tin and NaCl/KCl fluxes. They crystallize with the tetragonal ZrCuSiAs-type structure ($P4/nmm$, $Z = 2$), which was refined from single-crystal X-ray data of PrOsPO (a = 402.1(1), c = 824.0(1) pm, $wR2$ = 0.0490, 365 F^2) and ThAgPO (a = 396.1(1), c = 877.8(1) pm, $wR2$ = 0.0307, 314 F^2). They belong to a large family of isotypic compounds, of which several, mainly fluorine doped, iron containing compounds $Ln\text{FeAsO}_{1-x}\text{F}_x$ were discovered to be superconducting with relatively high transition temperatures only recently in other laboratories. Chemical bonding in these compounds is briefly discussed, and the importance of the weakly bonding Fe–Fe interactions for the phase transitions and the superconductivity is emphasized from the viewpoint of structural chemistry. A brief account of the history of the preparation of these compounds in our laboratory is given. Originally many of these compounds were obtained only in small amounts as byproducts in the course of the preparation of ternaries.

Key words: Rare Earth Compounds, Phosphides, Oxides, ZrCuSiAs-type Compounds

Introduction

The ZrCuSiAs-type structure was first described in 1974 as that of a “filled” PbFCl-type, where the copper atoms occupy tetrahedral voids formed by the arsenic atoms [1]. Subsequently, several chalcogenide oxides were reported, where the Cu positions of ZrCuSiAs are occupied by oxygen atoms, *e. g.* LaOAgS [2], LaOCuS [3], the series *R*CuSeO (*R* = Y, La, Sm, Gd) [4], *Ln*CuOTe (*Ln* = Ln, Ce, Nd) [5], and BiCuO*Ch* (*Ch* = S, Se, Te) [6 – 8]. Isotypic compounds with fluorine as the most electronegative component are also known: BaCuF*Ch* (*Ch* = S, Se) [9] and BaCuTeF [10]. Numerous reports deal with the optoelectronic properties of these materials.

Corresponding pnictide oxides have been investigated somewhat later, and the series of phosphide oxides *LnT*PO with *T* = Fe, Ru, Co [11], *T* = Mn [12], *T* = Zn [13−15], arsenide oxides *LnT*AsO with *T* = Mn [12], *T* = Zn [13], and *T* = Fe, Ru, Co [16], and antimonide oxides *LnT*SbO with *T* = Mn [12, 17], and *T* = Zn [17, 18], have been reported. In addition, five ZrCuSiAs-type pnictide oxides, where the Cu positions are occupied by Cd atoms have been characterized: LaCdPO and the series *Ln*CdAsO with *Ln* = La−Nd [19]. Furthermore, some pnictide oxides, where the actinoids thorium and uranium take the atomic positions of the lanthanoids, have been investigated, *e. g.* UCuPO [20], ThCuPO [21], UMnAsO [12], and ThCuAsO [21]. In the formulas of the pnictide oxides the oxygen atoms were placed at the end of the formulas in agreement with the nomenclature recommended by the International Union of Pure and Applied Chemistry (IUPAC). Until recently mainly the syntheses and the crystal chemistry of these pnictide oxides were studied. However, superconductivity reported for LaFePO [22] and LaNiPO [23, 24], both with transition temperatures of about 4 K, has raised interest in these compounds, which has accelerated since the finding of higher and higher transition temperatures of about 25 K in fluorine doped $\text{LaFeAs(O}_{\sim0.9}\text{F}_{\sim0.1})$ [25] and strontium doped $(\text{La}_{0.87}\text{Sr}_{0.13})\text{FeAsO}$ [26], of 36 K in $\text{GdFeAs(O}_{\sim0.83}\text{F}_{\sim0.17})$ [27], 41 K in $\text{CeFeAs(O}_{\sim0.84}\text{F}_{\sim0.16})$ [28], 43 K in $\text{SmFeAs(O}_{\sim0.85}\text{F}_{\sim0.15})$ [29], ∼ 48 K in $\text{NdFeAs(O}_{\sim0.88}\text{F}_{\sim0.12})$ [30], 52 K in $\text{PrFeAs(O}_{\sim0.88}\text{F}_{\sim0.12})$ [31], and 55 K in $\text{SmFeAs(O}_{\sim0.89}\text{F}_{\sim0.11})$ [32]. This interest in the ZrCuSiAs-type pnictide oxides has prompted us to look up our previous research results. We report here on 7 phosphide oxides with ZrCuSiAs-type structure, including two structure refinements, which up to now were difficult to access in the open literature, although we have presented most of these results at a conference [33]. In the meantime the compound CeOsPO has been reported independently [34].

Sample Preparation and Lattice Constants

Starting materials for the preparation of the rare earth metal containing ruthenium and osmium phosphide oxides *LnT*PO were ingots of the rare earth elements, all with nominal purities $> 99.9\,\%$. Filings of these were obtained under dried paraffin oil. They were washed with dried (sodium) *n*-hexane under argon to remove the oil. Elemental ruthenium and osmium as well as the oxides RuO_2 and OsO_2, all with nominal purities $> 99.9\,\%$, were in the form of powders. Solid pieces of red phosphorus had semiconductor quality (Hoechst, Knapsack: "ultra pure"). The equiatomic quaternary compounds can directly be prepared from these components, but they were obtained with higher yield and in better crystallized form from tin fluxes [35] using the starting atomic ratios $Ln : Ru(Os) : RuO_2(OsO_2) : P : Sn = 2:1:1:2:18$ with total weights of ~ 2 g. Good results were also achieved for the ruthenium compounds by first reacting small pieces of the rare earth elements and ruthenium directly in an arc melting furnace in an argon atmosphere. The thus obtained ingots of the overall composition "Ln_2Ru" were then ground to fine powders and reacted in a tin flux in the ratios $Ln_2Ru : RuO_2 : P : Sn = 1:1:2:12$. All of these mixtures were sealed under vacuum in silica tubes, kept for some h at the relatively low temperature of 500 °C to prevent violent reactions with the red phosphorus, and subsequently annealed for periods of about 2 weeks at temperatures of *ca.* 850 °C. The tin-rich matrix was then dissolved in diluted hydrochloric acid, which attacks the quaternary compounds at a smaller rate. Nevertheless, it is advisable to separate the quaternary compounds repeatedly from the reacting mixture, otherwise they may be dissolved as well.

The thorium silver compound ThAgPO was obtained inadvertently in the course of preparations aiming for new ternary thorium silver phosphides. Apparently, the oxygen was introduced during the handling of the air-sensitive samples. Filings from an ingot of thorium ($> 99.9\,\%$) were prepared as described above for the rare earth elements. They were mixed with powders of silver ($> 99.99\,\%$) and red phosphorus in the atomic ratio of $1:1:1$, pressed to a pellet and arc-melted. This resulted in a loss of phosphorus. For that reason additional phosphorus was added to the finely ground powder, and the mixture was placed in a silica tube, covered with a NaCl/KCl (1 : 1) salt flux, and sealed under vacuum. The total weight of the sample was approximately 1 g, of which 0.7 g resulted from the salt flux. After annealing for 10 days, the sample was quenched, and the flux was dissolved in water. In addition to Th_3P_4 and small amounts of ThO_2 the sample contained relatively large plate-like crystals with edge lengths of up to a few tenth of a mm (Fig. 1), which later on were found to have the composition ThAgPO.

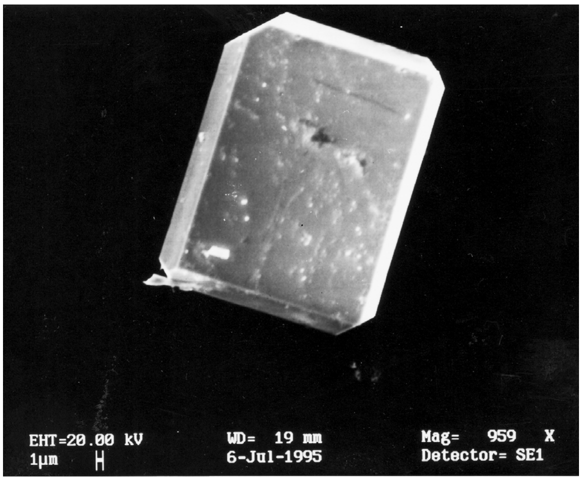

Fig. 1. A scanning electron micrograph of a ThAgPO crystal isolated from a NaCl/KCl flux. The large face of this tetragonal crystal has the indices (001), as identified in the course of the absorption correction for a similar crystal during the structure determination.

The quaternary products are stable in air for long periods of time. They are black, and in well crystallized form they show metallic luster. Energy-dispersive X-ray analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium. During earlier investigations of the isotypic compounds GdFePO, GdRuPO, CeCoPO, PrCoPO, and SmCoPO the oxygen content of the samples was proven by a scanning electron microscope with a windowless detector [11].

All products were characterized by Guinier powder diagrams using monochromatized Cu$K_{\alpha1}$ radiation with α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The proper assignment of indices was aided by comparing the observed patterns with theo-

Table 1. Lattice parameters of tetragonal ZrCuSiAs-type phosphide oxides as determined from Guinier powder diagrams.

Compound	*a* (pm)	*c* (pm)	c/a	*V* (nm^3)
TbRuPO	397.1(1)	792.7(2)	1.996	1.250
DyRuPO	396.3(1)	787.2(2)	1.987	1.236
LaOsPO	404.8(3)	840.8(6)	2.077	1.378
CeOsPO	402.8(1)	828.7(3)	2.057	1.345
CeOsPO [34]	403.1(1)	828.6(3)	2.056	1.346
PrOsPO	402.1(1)	824.1(2)	2.050	1.332
NdOsPO	401.0(1)	819.2(2)	2.043	1.317
SmOsPO	399.6(1)	806.9(3)	2.019	1.288
ThAgPO	396.6(1)	878.6(3)	2.215	1.382

retical ones [36]. The lattice constants (Table 1) are the results of least-squares fits.

Structure Refinements of PrOsPO and ThAgPO

Very small, well-shaped single crystals of PrOsPO and ThAgPO were selected for the structure determinations. Their quality for the X-ray data collection was checked on the basis of Laue diffractograms recorded on a precession camera with white Mo radiation. The X-ray intensity data were collected on an Enraf Nonius four-circle diffractometer (CAD4) with graphite-monochromatized MoK_α radiation and a scintillation counter with pulse-height discrimination. The scans were along the diffraction streaks ($\theta/2\theta$) with background counts at both ends of each scan. For both crystals the whole reciprocal sphere was measured. Factors for numerical absorption corrections were obtained by optimizing the crystal shapes by comparison of equivalent reflections.

The isotypy of the crystals with that of ZrCuSiAs was already known from previous investigations and from the powder data. The high Laue symmetry was confirmed prior to the data averaging, and the positional parameters of PrFeAsO [11] were used as starting parameters for the structure refinements with a full-matrix least-squares program [37] 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 extinction was optimized as a least-squares variable.

As a check for the composition we refined occupancy values together with variable anisotropic displacement parameters. This was possible because we had been collecting diffraction data up to rather high 2θ values (Table 2). The results were as follows (in % occupancy): Pr 99.9(2), Os 100.3(1), P 99.0(9), O 106(2); Th 99.2(2), Ag 99.2(3), P 97(1), O 106(3). Thus, practically all occupancy parameters were within 3 standard deviations at the ideal values; especially also those of the oxygen atoms. We considered the possibility of nitrogen as an impurity at the oxygen position, although up to now no nitrogen-containing ZrCuSiAs-type compound has been reported. For nitrogen at the oxygen position an occupancy value of about 87% could be expected. Since the oxygen positions for both data sets were found to have considerably higher occupancy values, we concluded that any nitrogen content of the samples is not essential for the stability of these compounds.

Table 2. Crystal data and structure refinement for PrOsPO and ThAgPO, ZrCuSiAs-type, space group $P4/nmm$ (no. 129), $Z = 2$.

Empirical formula	PrOsPO	ThAgPO
Molar mass units	378.08	386.88
a, pm	402.06(6)	396.06(7)
c, pm	823.97(9)	877.79(10)
V, nm^3	1.3320	1.3769
Calculated density, $g\,cm^{-3}$	9.43	9.33
Crystal size, μm	$10 \times 30 \times 30$	$10 \times 50 \times 60$
Transm. ratio (max/min)	3.02	3.97
Absorption coefficient, mm^{-1}	66.0	61.6
F(000), E	316	320
Range in 2θ	4° to 90°	4° to 84°
Range in *hkl*	$\pm7, \pm7, \pm16$	$\pm7, \pm7, -12 \rightarrow +15$
Total no. reflections	4277	2594
Independent reflections	365	314
R_{int}	0.068	0.033
Reflections with $I \geq 2\sigma(I)$	330	300
R_σ	0.024	0.017
Data / parameters	365 / 12	314 / 12
Goodness-of-fit on F^2	0.845	1.155
Final *R* indices $[I \geq 2\sigma(I)]$		
$R1$	0.022	0.014
$wR2$	0.049	0.032
R indices (all data)		
$R1$	0.028	0.016
$wR2$	0.055	0.031
Extinction coefficient	0.0148(12)	0.0172(10)
Largest diff. peak and hole, e Å^{-3}	3.69 / −4.88	1.79 / −2.94

During the final least-squares cycles the ideal occupancy values were used. The final residuals are summarized in Table 2. The positional atomic parameters and the interatomic distances are listed in the Tables 3 and 4.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de

Table 3. Atomic positions and isotropic displacement parameters (pm^2) of PrOsPO and ThAgPO. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	$P4/nmm$	x	y	z	U_{eq}
PrOsPO					
Pr	2*c*	1/4	1/4	0.14344(6)	56(1)
Os	2*b*	3/4	1/4	1/2	48(1)
P	2*c*	1/4	1/4	0.6473(3)	50(3)
O	2*a*	3/4	1/4	0	80(10)
ThAgPO					
Th	2*c*	1/4	1/4	0.15459(3)	46(1)
Ag	2*b*	3/4	1/4	1/2	104(1)
P	2*c*	1/4	1/4	0.7021(2)	63(3)
O	2*a*	3/4	1/4	0	62(7)

Table 4. Interatomic distances of PrOsPO and ThAgPO as calculated with the lattice parameters from the powder data. All distances up to 395 pm (metal atoms), 320 pm (P), and 280 pm (O) are listed. Standard deviations are all equal to or smaller than 0.2 pm.

PrOsPO			ThAgPO		
Pr:	4O	233.2	Th:	4O	240.3
	4P	332.5		4P	307.3
	4Os	356.0		4Ag	362.6
	4Pr	369.8		4Th	390.4
Os:	4P	234.8	Ag:	4P	266.4
	4Os	284.3		4Ag	280.4
	4Pr	356.0		4Th	362.6
P:	4Os	234.8	P:	4Ag	266.4
	4Pr	332.5		4Th	307.3
O:	4Pr	233.2	O:	4Th	240.3

/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-419464 (PrOsPO) and CSD-419463 (ThAgPO).

Discussion

With the presently reported seven quaternary phosphide oxides the number of ZrCuSiAs-type pnictide and chalcogenide oxides has increased to well over one hundred. In view of the current activity in connection with the superconductivity of some of these compounds it can be expected that soon many more isotypic compounds will be prepared with similar compositions, *e. g.* by substituting oxygen with nitrogen or fluorine, and with appropriate valence compensation at the metal sites.

In Fig. 2 the new compounds are represented by their unit cell volumes together with their homologous iron and ruthenium compounds reported earlier [11]. It can be seen that the volumes of the osmium compounds are slightly larger than those of the corresponding ruthenium compounds, as is usually the case [38].

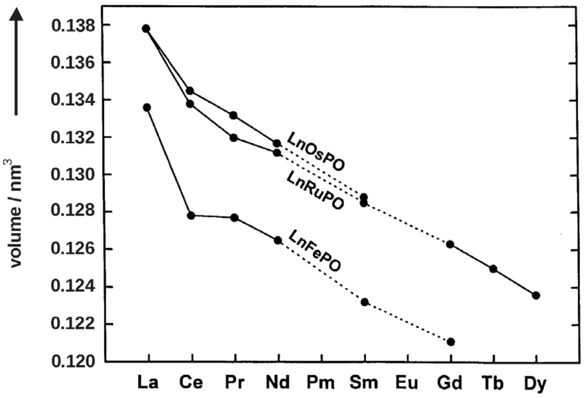

Fig. 2. Cell volumes of the new ruthenium- and osmium-containing rare earth phosphide oxides with ZrCuSiAs-type structure as compared to earlier reported [9] isotypic iron and ruthenium compounds.

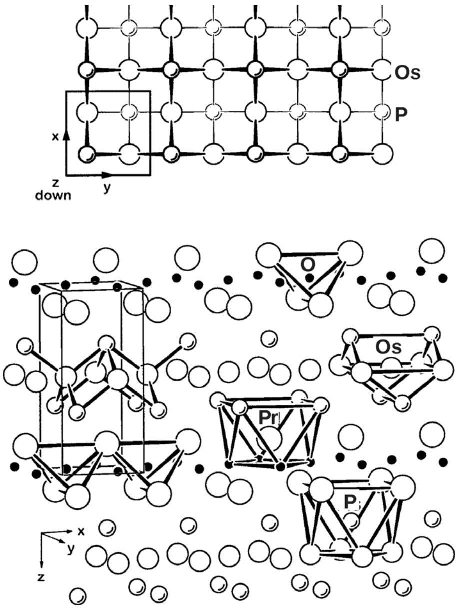

Fig. 3. Crystal structure of PrOsPO and near-neighbor coordinations. The upper part shows the two-dimensionally infinite osmium phosphorus polyanion as projected along the tetragonal axis. In this projection only the strong Os–P interactions are emphasized. The complete coordination of an Os atom with its square-like Os environment is shown in the lower part.

For instance, in the series of the filled skutterudite phosphides $Ln\mathrm{Os}_4\mathrm{P}_{12}$ and $Ln\mathrm{Ru}_4\mathrm{P}_{12}$ [39] the cell volumes of the osmium compounds are larger by 1.8 % on average. Here, with the series of *Ln*OsPO and *Ln*RuPO the cell volumes of the Os and Ru compounds differ by between 0.1 % and 0.9 % for the La and Pr containing compounds, respectively. These minor inconsistencies may be ascribed to differences in the preparation procedures and to small homogeneity ranges of the compounds.

In the series of the iron compounds *Ln*FePO the cell volume of the cerium compound deviates from the smooth function, in contrast to the cell volumes of the cerium compounds in the other two series *Ln*RuPO and *Ln*OsPO. This indicates that the fourth valence electron of the cerium atoms is more delocalized in CeFePO than in CeRuPO and CeOsPO.

In Fig. 3 we show the ZrCuSiAs-type structure of PrOsPO with the near-neighbor environments of the four different atomic sites. Chemical bonding in the ZrCuSiAs-type pnictide oxides has been discussed earlier in several reports, for instance for PrFePO [11] and PrFeAsO [16]. For the presently characterized compounds PrOsPO and ThAgPO it can be rationalized to a first approximation with the expected valences for the rare earth, thorium, phosphorus, and oxygen atoms with Pr^{+3}, Th^{+4}, P^{-3}, and O^{-2}. As a result, the iron and silver atoms obtain the oxidation numbers $+2$ and $+1$, respectively. In view of the somewhat layered character of the structure, in a first approximation one may write the formulas as $[PrO]^{+1}[OsP]^{-1}$ and $[ThO]^{+2}[AgP]^{-2}$. However, it must be emphasized that the assignment of oxidation numbers should not imply ionic bonding. Certainly, the bonding within the two-dimensionally infinite $[OsP]^{-1}$ and $[AgP]^{-2}$ layers is essentially covalent (strong interactions of the orbitals of the valence electrons within these layers), and to a lesser degree within the two-dimensionally infinite $[PrO]^{+1}$ and $[ThO]^{+2}$ layers. Also, the interactions between these alternating stacks have some covalent character, even though they may be considered as predominantly ionic. In total, the interactions between the alternating layers contribute considerably to the bonding energy of these compounds. Thus, it is somewhat misleading to describe these ZrCuAsSi-type compounds as layered, implying connotations to the well known lubricants graphite and molybdenum disulfide MoS_2. In contrast, the bonding between the topological layers $[PrO]^{+1}$ and $[FeAs]^{-1}$ and even more so between the layers $[ThO]^{+2}$ and $[AgP]^{-2}$ is rather strong. The compounds are brittle and do not show a tendency for cleavage.

In view of the exciting superconducting behavior of the iron arsenide oxide series *Ln*FeAsO we look again at the atomic environment of the iron atoms, which are situated in distorted tetrahedra formed by the P atoms in the *Ln*FePO series, and by the As atoms in the compounds *Ln*FeAsO. However, we have emphasized repeatedly in the discussions of chemical bonding of these rare earth transition metal pnictide oxides *LnTPn*O [11 – 13, 16, 18] that the $T-T$ distances in these tetragonal compounds – readily calculated from the lattice constant a by division with $\sqrt{2}$ – are short enough to be considered as weakly bonding and must not be neglected. Such interactions – Fe–Fe for LaFeAsO – are very likely responsible for the 150 K anomaly of that compound and may as well play a key role in the superconductivity of these pnictides oxides [25, 40 – 43, and references therein]. At relatively high temperatures the Fe atoms are situated in the centers of their coordination polyhedra forming four weak Fe–Fe bonds to their four Fe neighbors surrounding the central Fe atom in the form of a square. At lower temperatures, the weak Fe−Fe bonding may lead to Jahn-Teller-like distortions resulting in Fe–Fe bonded chains or clusters.

This situation is somewhat similar to the well-known metal-insulator phase transition in vanadium dioxide VO_2, with rutile (TiO_2)-type structure in the high-temperature form. The V atoms are in the oxidation state $+4$ and form a chain with rather weak V–V bonds at equal distances in the high-temperature modification. In the low-temperature modification the vanadium atoms have alternating short and long V–V distances, thus forming V_2 pairs. Thus, the fifth valence electrons of the vanadium atoms are delocalized in the high-temperature form with metallic conductivity, whereas in the low-temperature form they are localized within the V_2 pairs. This leads to a doubling of that translation period which corresponds to the tetragonal axis of the rutile structure.

For the Fe atoms in the structures of the *Ln*FeAsO series, the situation is similar, but more complicated. They have four close iron neighbors within their square grids and thus they have more options to condense to various Fe–Fe bonded units when the temperature is lowered. Apparently, the doping with fluorine in the high-T_c superconducting componds $LnFeAsO_{1-x}F_x$ not only provides more conduction electrons. The local disorder of fluorine and oxygen atoms also suppresses the phase transition and thus enables the conduction electrons to stay at the Fermi surface, thereby providing the opportunity for superconductivity.

In concluding, we wish to give a brief summary of the history of the preparation and characterization of these newly discovered series of superconducting phosphide oxides *LnT*PO in Münster. Many of these were obtained first as byproducts of preparations while aiming at ternary compounds within the systems *Ln*-*T*-P. Such samples were usually prepared from a tin flux [35]. Any oxygen present in the starting materials or introduced during the handling of such samples was readily incorporated to form the quaternary compounds *LnT*PO. These compounds have X-ray powder patterns corresponding to the tetragonal PbFCl-type structure, where the heavy atoms of the compounds *LnT*PO occupy the atomic positions of the PbFCl-type structure. The light oxygen atoms of the new compounds contribute little to the scattering, and therefore the agreement between the experimental patterns of the compounds *LnT*PO and the patterns calculated for the hypothetical compounds *LnT*P was usually quite good. However, since the compounds were usually obtained only in small amounts and in the form of microcrystalline powders we did not publish them, except for one case, which we had corrected later on [11]. It was only when we succeeded in obtaining a single crystal of UCuPO [20] that the structure refinement showed that the compound has a "filled" PbFCl structure, *i. e.* a ZrCuSiAs-type structure. By intentionally adding oxygen we have subsequently prepared most of these compounds in good yield, and many of these also in well crystallized form suited for single-crystal structure determinations. One of these was LaFePO, which we characterized also by magnetic susceptibility measurements carried out by K. Hartjes. The results were never published in the easily accessible literature, but they are contained in a small chapter entitled "Der Supraleiter LaFePO" in the thesis of B. I. Zimmer [44]. The transition temperature was found at 3.8 K, where on cooling the Pauli paramagnetism rapidly disappears, and the compound becomes diamagnetic. We did not follow up with electrical conductivity measurements to confirm this result. After all, a transition temperature below liquid He temperature is not that exciting. Earlier, the structurally closely related compound $LaRu_2P_2$had been reported to be a superconductor below 4.1 K [45] and this finding also has not raised much interest in the superconductor community. It was only very recently, when the relatively high-T_c superconductivity of the doped material $LaFeAs(O_{\sim0.9}F_{\sim0.1})$ excited so many researchers around the world, that we realized how close we had been to a real discovery. Without the work of Kamihara *et al.* [22, 25], we still would not know. By the way, LaFePO is sometimes reported to be only the second iron compound to be found superconducting, after $LaFe_4P_{12}$ [39, 46]. This is not quite true. We had reported Y_2FeC_4 to become a superconductor below 3.6 K [47], and this finding did not arise much interest either.

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