Thermo-chemical properties and electrical resistivity of Zr-based arsenide chalcogenides

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Abstract

Ternary phases in the systems Zr–As–Se and Zr–As–Te were studied using single crystals of ZrAs\textsubscript{x1.40(1)}Se\textsubscript{0.50(1)} and ZrAs\textsubscript{x1.60(2)}Te\textsubscript{0.40(1)} (PbFCl-type of structure, space group \textit{P}4/\textit{nmm}) as well as ZrAs\textsubscript{0.70(1)}Se\textsubscript{1.30(1)} and ZrAs\textsubscript{0.75(1)}Te\textsubscript{1.25(1)} (NbPS-type of structure, space group \textit{Immm}). The characterization covers chemical compositions, crystal structures, homogeneity ranges and electrical resistivities. At 1223 K, the Te-containing phases can be described with the general formula ZrAs\textsubscript{x}Te\textsubscript{2} with 1.53(1) \textless x \textless 1.65(1) (As-rich) and 0.58(1) \textless x \textless 0.75(1) (Te-rich). Both phases are located directly on the tie-line between ZrAs\textsubscript{2} and ZrTe\textsubscript{2}, with no indication for any deviation. Similar is true for the Se-rich phase ZrAs\textsubscript{x}Se\textsubscript{2} with 0.70(1) \textless x \textless 0.75(1). However, the compositional range of the respective As-rich phase ZrAs\textsubscript{x−y}Se\textsubscript{2−x} (0.03(1) \textless y \textless 0.10(1); 1.42(1) \textless x \textless 1.70(1)) is not located on the tie-line ZrAs\textsubscript{2}–ZrSe\textsubscript{2}, and exhibits a triangular region of existence with intrinsic deviation of the composition towards lower non-metal contents. Except for ZrAs\textsubscript{0.75(1)}Se\textsubscript{1.25(1)}, from the homogeneity range of the Se-rich phase, all compounds under investigation show metallic characteristics of electrical resistivity at temperatures \textless 20 K. Related uranium and thorium arsenide selenides display a typical magnetic field-independent rise of the resistivity towards lower temperatures, which has been explained by a non-magnetic Kondo effect. However, a similar observation has been made for ZrAs\textsubscript{1.40(1)}Se\textsubscript{0.50(1)}, which, among the Zr-based arsenide chalcogenides, is the only system with a large concentration of intrinsic defects in the anionic substructure.

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1. Introduction

The electrical resistivity $\rho(T)$ of an ordinary metal decreases monotonically with decreasing temperature and becomes constant at low temperatures. In contrast, the resistivity of metals with certain dilute magnetic impurities exhibits a shallow minimum at low temperatures \cite{1}. This anomaly in $\rho(T)$ is a characteristic feature of the Kondo effect and is associated with exchange scattering of the conduction electrons of magnetic impurities \cite{2}. A Kondo-type phenomenon is also expected for scattering species with non-magnetic internal degrees of freedom, such as structural two-level systems. The influence of a magnetic field on the non-magnetic Kondo effect should be very weak and, therefore, distinctly different from the destruction of the magnetic Kondo effect by a comparatively low magnetic field \cite{3}.

Our previous works point to intrinsic structural disorder in single crystals of the PbFCl-type arsenide selenides UAsSe, ThAsSe and ZrAs\textsubscript{1.40}Se\textsubscript{0.50}, as inferred from X-ray and electron diffraction as well as transmission electron microscopy studies \cite{4,5}. This structural disorder is held responsible for the formation of two-level systems that are the cause of glass-type temperature dependences of both the thermal conductivity and the specific heat in the millikelvin temperature range \cite{6}. Most interestingly, the electrical resistivities of UAsSe, ThAsSe and ZrAs\textsubscript{1.40}Se\textsubscript{0.50}
show a low-temperature upturn, whose magnitude is unaffected by the application of a magnetic field. These observations are considered as evidence for a non-magnetic Kondo effect derived from structural disorder.

In order to clarify the underlying mechanism, especially the microscopic nature of the two-level systems, we have extended our studies to further Zr-based arsenide selenides and tellurides [5,7]. These non-actinide systems have significant advantages in comparison with ThAsSe. Large single crystals can be grown via chemical transport reaction (CTR) in higher purity since Zr species, when compared with Th ones, are less reactive against silica, which is used as ampoule material. The resulting Zr-based compounds can be favourably studied by X-ray and neutron diffraction techniques. The form factor and the scattering length relations are advantageous in comparison with the uranium and thorium systems. Here we present a detailed study of the systems Zr–As–Se and Zr–As–Te.

2. Experimental

2.1. Synthesis

Due to the thermo-chemical properties of the constituents of the systems Zr–As–Se and Zr–As–Te (high pnictide and chalcogenide partial pressures) and the concurrent possibility of forming volatile iodides of zirconium, the CTR technique presents a suitable method for crystal growth of the target compounds. In particular, for compounds that decompose during melting, showing phase transformations or high decomposition pressures at their melting point, the CTR is an alternative to crystal growth in a heterogeneous reaction, creating a gaseous species. Subsequent to the materials’ transport, a reformation takes place. The driving force for the materials’ transport between the dissolution and deposition sides is a thermodynamic potential gradient. Most often this is achieved by temperature differences. Ternary compounds in the systems Zr–As–Se and Zr–As–Te have first been synthesized by direct reaction of the elements zirconium (Goodfellow, 99.2 wt%, powder, content of Hf: 2500 ppm), arsenic (Chempur, 99.999 wt%), selenium (Chempur, 99.999 wt%), and tellurium (Chempur, 99.9999 wt%) at 1223 K in evacuated fused silica ampoules during 1 week. Starting from the microcrystalline powders, the ternary compounds are crystallized by exothermal transport reactions in temperature gradients from 1123 K (source) to 1223 K (sink). As the reactants may attack the silica, which can lead to silicon contaminations of the products, we additionally inserted a glassy carbon tube into the silica tube for the syntheses in the Zr–As–Se system.

2.2. Characterization

Single crystals obtained by the CTR were characterized by electron probe microanalysis (EDXS, PHILIPS XL 30), wavelength-dispersive X-ray spectroscopy (WDXS, CAMECA SX 100), single-crystal (RIGAKU, AFC 7) and powder X-ray diffraction (Huber Image Plate Guinier camera G670), as well as by chemical analyses applying the inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian, VISTA RL) method. The samples were checked for their N, O and C contents using the carrier gas hot extraction and combustion methods, respectively (N, O: LECO TCH 600; C: LECO C-200).

For WDXS investigations, selected single crystals were embedded coplanarly to a well-formed prism face and processed metallographically. The WDXS method was calibrated by relevant element standards. It could be shown that the investigated crystals were chemically homogeneous and did not contain any constituents of the transport agent or traces of silicon.

For the ICP-OES analyses, suitable digestion reagents and digestion conditions for the precise and simultaneous determination of zirconium, arsenic, selenium/tellurium and impurities like iron or hafnium were at first ascertained by pre-investigations on the microcrystalline materials. After that, single crystals (each between 2 and 10 mg) were digested in a mixture of HNO3 conc. (2 ml) and HF conc. (20 µl per 5 mg of weighted-in quantity). The concentration of HF needed to completely dissolve the samples was low enough for the measurements to be carried out with the usual glass equipment (concentric nebulizer, twister-cyclotron spray chamber, quartz torch with an alumina injector tube). In any case, the chemical compositions determined by ICP-OES agreed very well with the results of the corresponding WDXS measurements (Table 1).

### Table 1

| System/method | Zr (at%) | As (at%) | Se (at%) | Te (at%) | Resulting chemical composition |
|---------------|---------|---------|---------|---------|------------------------------|
| Zr–As–Se      |         |         |         |         |                              |
| WDXS          | 34.67(4)| 48.51(5)| 16.80(2)| –       |                             |
| ICP-OES       | 33.8(3) | 47.8(6) | 17.5(5) | –       | Zr1.00(7)As1.38(1)Se0.50(1)  |
| WDXS          | 33.1(1) | 23.74(6)| 43.2(1) | –       | Zr1.00(5)As0.73(3)Se1.30(7)  |
| ICP-OES       | 33.1(3) | 23.6(4) | 43.3(4) | –       | Zr1.00(1)As0.71(4)Se1.31(1)  |
| Zr–As–Te      |         |         |         |         |                              |
| WDXS          | 33.4(7) | 53.3(7) | –       | 13.3(3) | Zr1.00(2)As1.60(2)Te0.40(1)  |
| ICP-OES       | 33.6(3) | 53.3(3) | –       | 13.2(3) | Zr1.00(8)As1.59(1)Te0.39(6)  |
| WDXS          | 33.2(3) | 25.2(2) | –       | 41.7(2) | Zr1.00(6)As0.75(6)Te1.25(5)  |
| ICP-OES       | 33.5(1) | 24.89(5)| –       | 41.6(2) | Zr1.00(3)As0.74(4)Te1.24(6)  |
A significant side reaction with the glassy carbon tube could be excluded: the concentration of carbon was not more than 0.037(5) wt% after a typical heat treatment for 1 week at 1273 K. The samples were also checked for other impurities (average concentration): N ≤ 0.05 wt%, O ≤ 0.5 wt%, Hf ≤ 0.1 wt%, Si ≤ 0.1 wt% and Fe ≤ 0.02 wt%.

For electrical resistivity measurements on the Te-rich phase ZrAs_{1−y}Te_{2−x} (y = 0; 0.58 ≤ x ≤ 0.75), a single crystal with the chemical composition Zr_{1.000(6)}As_{0.595(4)}Te_{1.416(5)} (WDXS, Zr: 33.2(3) at%; As: 19.8(1) at%; and Te: 47.0(2) at%) was selected.

2.3. Determination of phase equilibria in the ternary systems

Isothermal sections of the ternary phase diagrams Zr–As–Se and Zr–As–Te at 1223 K close to the tie-lines ZrAs_{2−y}Se_{2−x} and ZrAs_{2−y}Te_{2−x} were determined via two different experimental techniques, namely CTR and mineralization annealing experiments. Crystals with chemical compositions of the borders of the corresponding homogeneity ranges were synthesized via CTR using iodine (5 wt% of initial sample mass) as transport agent, and by starting from pre-reacted powder material (see section synthesis). In these cases, the chemical composition of the starting materials was chosen between the ternary homogeneity range and the corresponding binary compound. Microcrystalline powders with defined chemical compositions within the homogeneity ranges were synthesized using isothermal mineralization annealing experiments, starting from the elements Zr, As and Se (Te), with the addition of a small amount of iodine acting as mineralizer (0.5 wt% of sample mass) in glassy carbon crucibles enclosed in silica ampoules. In both cases, CTR as well as isothermal annealing mineralization (1223 K), the chemical compositions of the resulting crystals were determined by WDXS.

2.4. Physical measurements

The electrical resistivity along the shortest crystallographic axis of various Zr-based arsenide selenides and tellurides was investigated by a conventional four-point ac method utilizing a commercial set-up (PPMS, Quantum Design). In the case of ZrAs_{1.40}Se_{0.50}, measurements have been extended to 0.12 K using a 3He–4He dilution refrigerator equipped with an LR-700 ac resistance bridge. Electrical contact pads were made by electrochemical deposition of copper.

3. Results and discussion

3.1. Phase equilibria

In the system Zr–As–Se, two ternary phases with general compositions Zr(As,Se)_{2} are known (non-metal/metal atomic ratio ≈ 2) [5]. The arsenic-rich phase ZrAs_{x−y}Se_{2−x} (0.03(1) ≤ y ≤ 0.10(1); 1.42(1) ≤ x ≤ 1.70(1)) exhibits a large homogeneity range. Because of a significant arsenic deficiency y for this phase in the complete homogeneity range, the non-metal/metal atomic ratio is smaller than 2. The border compositions for the approximately triangular-shaped homogeneity range are ZrAs_{1.67(1)}Se_{0.30(1)} for the As-richest phase, ZrAs_{1.37(1)}Se_{0.58(1)} for the Se-richest phase and ZrAs_{1.40(1)}Se_{0.50(1)} for the Zr-richest point (see inset of Fig. 1). According to analytical data (WDXS) the selenium-rich crystals ZrAs_{x−y}Se_{2−x} (y = 0, 0.70(1) ≤ x ≤ 0.75(1)) have a non-metal/metal atomic ratio of exactly 2 for all compositions within the homogeneity range ZrAs_{1.37(1)}Se_{0.58(1)} (y = 0; 1.53(1) ≤ x ≤ 1.65(1)) and the selenium-rich phase (4), large homogeneity range) ZrAs_{x−y}Te_{2−x} (y = 0; 0.58(1) ≤ x ≤ 0.75(1)). Both phases are located directly on the tie-line between ZrAs_{2} and ZrTe_{2}, with no significant extension in any other direction. Rhombohedral phase Zr_{2.3}AsTe_{2} (5), reported in [8].
range, which means that this range is located directly on the tie-line between ZrAs₂ and ZrSe₂ (Fig. 1a).

In the system Zr–As–Te, the two ternary phases under consideration are characterized by the general formula ZrAsₓ₁₋ₓTe₂–ₓ with 1.53(1) ≤ x ≤ 1.65(1) (arsenic-rich) and 0.58(1) ≤ x ≤ 0.75(1) (tellurium-rich). Accordingly, both phases are directly located on the tie-line between ZrAs₂ and ZrTe₂ and, thus, show no tendency of non-metal/metal ratio ≠ 2 (Fig. 1b). Additionally, Zr₂.₃AsTe₂ (Ta₂S₂C-type of structure) was reported as a further ternary compound in this system \[8\], but no information on homogeneity ranges is available.

Comparison of the Zr arsenide chalcogenides (chalc. = Se, Te) shows that the As-rich selenide phase ZrAsₓ₁₋ₓSe₂–ₓ (0.03(1) ≤ y ≤ 0.10(1); 1.42(1) ≤ x ≤ 1.70(1)) realizes a unique situation with As-deficit. In the following, the crystal chemical relevance of this As-deficit will be analysed and it will be shown that this phase also exhibits a unique behaviour in some of its physical properties.

### 3.2. Crystal structures

The arsenic-rich compounds ZrAsₓ₁₋ₓSe₂–ₓ (0.03(1) ≤ y ≤ 0.10(1); 1.42(1) ≤ x ≤ 1.70(1)) and ZrAsₓ₁₋ₓTe₂–ₓ (y = 0; 1.53(1) ≤ x ≤ 1.65(1)) crystallize in the tetragonal PbFCl-type of structure (branch of the ZrSSi-type, space group \(P4/nmm\), No. 129). The larger anions typically occupy a 2c site, while the smaller anions take the 2a site. The anions may principally be distributed on both sites in the sense of substitution. In the case of ZrAs₀.₉₀(₁)Se₀.₅₀(₁)As₀.₅₀ with unit cell parameters \(a = 374.69(1)\) pm and \(c = 807.16(1)\) pm, the 2c site is equally occupied by Se/As, and there is a deficiency in the quadratic arsenic layer at site 2a [5]. The compound ZrAs₁.₆₀(₂)Te₀.₄₀(₁) with unit cell parameters \(a = 383.83(1)\) pm and \(c = 819.78(2)\) pm also shows a mixed occupied 2c site, but no significant deficiency within the quadratic arsenic layer at site 2a (Fig. 2a).

The corresponding selenium-rich phase ZrAsₓ₁₋ₓSe₂–ₓ (0.70(1) ≤ x ≤ 0.75(1)) and the tellurium-rich phase...
ZrAs₅Te₂₋ₓ (0.58(1) ≤ x ≤ 0.75(1)) crystallize in the orthorhombic NbP₅S₆-type of structure (space group Immm, No. 71). ZrAs₀.70(1)Se₁.30(1) (unit cell parameters a = 369.50(2) pm, b = 524.32(2) pm, c = 1260.21(5) pm) and ZrAs₀.75(1)Te₁.25(1) (unit cell parameters a = 377.61(1) pm, b = 564.09(2) pm, c = 1335.61(4) pm) contain As/Se (As/Te) mixed occupied linear chains with alternating distances (d(As–As) = 277.8 pm and 287.4 pm) running along [0 1 0] as well as fully occupied, corrugated double layers of zirconium and selenium/tellurium (Fig. 2b). The semiconductor-like electrical transport properties of the selenium-rich phase (see next paragraph) hint to a possible formation of homonuclear bonds (i.e. As–As dumbbells) between arsenic within the chains along [0 1 0] in combination with isolated Se²⁻ ions.

3.3. Physical properties

As discussed previously, above T ≈ 20 K tetragonal ZrAs₁.₄₀(1)Se₀.₅₀(1) behaves like an ordinary metal [5]. The small linear (Sommerfeld) coefficient γ of the specific heat of 1.7 mJ mol⁻¹ K⁻² and a very small paramagnetic dc susceptibility, being overcompensated by the diamagnetic contribution, reflect the small electronic density of states at the Fermi level. None of the physical properties measured reveals any phase transition in the temperature range 2–300 K. Indeed, at elevated temperature (T > 20 K), the ρ(T) dependence along the a-axis of ZrAs₁.₄₀(1)Se₀.₅₀(1) (Fig. 3a) can well be described by a generalized Bloch–Grüneisen–Mott relation with n = 3 (see Ref. [5] for more details). On the other hand, the large residual resistivity ρ₀ = 140 μΩ cm K⁻¹ (and the residual resistivity ratio, RRR, being as small as 1.15) points to significant structural disorder that is also evident from both electron probe microanalysis and X-ray diffraction studies (vide supra). It is remarkable that, below T ≈ 20 K, an additional temperature-dependent contribution to the resistivity has been observed in many ZrAs₁.₄₀Se₀.₅₀ single crystals studied so far. Details are depicted in the inset of Fig. 3a. Here, the low-temperature ρ(T) data are shown as Δρ/ρ₀ vs T¹/². Note that a very similar, magnetic-field-independent –AT¹/² term has also been found in the isostructural phase ThAsSe [6].

Figs. 3b–d present the temperature dependence of the electrical resistivities measured along [1 0 0] for other Zr-based arsenide selenides and tellurides. While the orthorhombic phase ZrAs₀.₇₅(1)Se₁.₂₅(1) displays a large negative temperature coefficient to the resistivity in the whole temperature range, ρ(T) of ZrAs₁.₆₀(1)Te₀.₄₀(1) and ZrAs₀.₅₈(1)Te₁.₄₂(1) shows well-defined metallic behaviour (from various specimens of the orthorhombic Te-rich phase, only a sample with x = 0.58 was large enough to perform the resistivity measurements along the a axis). The ρₐ(T) data of both tellurides can be described in a similar way as those of ZrAs₁.₄₀(1)Se₀.₅₀(1), including a correction due to s–d interband electron scattering for tetragonal ZrAs₁.₆₀(2)Te₀.₄₀(1). The fitting parameters are listed in the caption of Fig. 3. Although both tellurides display a low value of RRR (1.85 and 1.59 for ZrAs₁.₆₀(2)Te₀.₄₀(1) and ZrAs₀.₅₈(1)Te₁.₄₂(1), respectively), their residual resistivity is significantly smaller than that of ZrAs₁.₄₀(1)Se₀.₅₀(1). This experimental finding is in good agreement with the crystallographic data that point at less structural disorder in the tellurides than in the selenides. Most interestingly,
however, no additional contribution to the low-temperature resistivity has been detected for either tetragonal ZrAs$_{1.60(2)}$Te$_{0.40(1)}$ or orthorhombic ZrAs$_{0.58(1)}$Te$_{1.42(1)}$.

4. Summary

To conclude, we have investigated a single crystal with the chemical composition ZrAs$_{1.40}$Se$_{0.50}$ from the homogeneity range of the PbFCl-type phase ZrAs$_{x-y}$Se$_{2-x}$ (0.03(1) $\leq y \leq 0.10(1)$; 1.42(1) $\leq x \leq 1.70(1)$), whose low-temperature resistivity shows a $-AT^{1/2}$ contribution. The isostructural phase ZrAs$_{1.60}$Te$_{0.40}$ and the corresponding chalcogenide-rich NbPS-type compounds, ZrAs$_{0.70}$Se$_{1.30}$ and ZrAs$_{0.58}$Te$_{1.42}$, do not show any low-temperature anomaly in the electrical resistivity. It is remarkable that the homogeneity ranges of the latter phases extend directly on the tie-lines of the corresponding binary border phases with no indication of any deviation, i.e., no tendency to a lower non-metal content. In contrast, the results of the X-ray diffraction investigations as well as the chemical analysis of ZrAs$_{1.40}$Se$_{0.50}$ point to an exceptional homogeneity range. Defects in the As-layers illustrate that low-energy excitations of the electron gas might be triggered by the formation of As-oligomers and/or by the mixed occupation of the 2c sites by arsenic and selenium. However, the role of the mixed occupation of the 2c sites by arsenic and selenium needs further explanations.

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