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Bulk properties of single crystals of the valence-unstable compound SmRh$_2$Si$_2$

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Abstract

We present the crystal growth as well as the structural, chemical and physical characterization of SmRh$_2$Si$_2$ single crystals. Their ground state is antiferromagnetically, as indicated by the behaviour of the magnetic susceptibility and the specific heat at the second order phase transition observed at $T_N = 64$ K. The Sommerfeld coefficient is small and similar to that of LuRh$_2$Si$_2$ with $\gamma_0 \approx 7$ mJ/(molK$^2$). Susceptibility measurements show no Curie-Weiss behaviour at high temperatures which is a consequence of the large Van-Vleck contribution of the excited multiplets of Sm$^{3+}$. Previous angle-resolved photoemission studies showed that at 10 K, the valence of the Sm ions is smaller than three at the surface as well as in the bulk, suggesting a possible Kondo screening of the Sm$^{3+}$ ions. This could not be observed in our thermodynamic and transport measurements.

1. Introduction

Sm-based compounds have been studied rarely in the past compared to compounds containing lanthanide ions like Ce, Eu, Gd, Ho or Yb, but the recent discovery of topologically insulating behaviour in SmB$_6$ [1–3] renewed the interest in the community in Sm-based compounds. Some Sm compounds exhibit strongly correlated electron behaviour like the heavy-fermion compounds SmOs$_4$Sb$_{12}$ [4] or SmTi$_2$Al$_2$ [5], which have a complex crystallographic structure and the characterization of systems with lower structural complexity is highly desired. Recently, the valence of the Sm ions in SmRh$_2$Si$_2$ single crystals was studied by angle resolved photoemission spectroscopy (ARPES). Contributions from the bulk as well as from the surface to the photoemission spectrum have been determined [6]. Divalent Sm 4f contributions to the photoemission spectrum are expected close to the Fermi level and have been observed experimentally in the past for Sm metal [7] and a number of Sm compounds [8, 9]. Such emissions from divalent Sm were mostly identified as surface valence transitions in trivalent bulk systems. ARPES revealed that for Sm ions in SmRh$_2$Si$_2$, the electronic properties of bulk and surface are rather similar and the Sm ions behave in both cases slightly mixed valent. The mean valence of the Sm ions in SmRh$_2$Si$_2$ was estimated to be about 2.94 at $T = 10$ K [6]. Usually, the valence of Sm ions at the surface of a single crystal is 2+ and the observed deviation is quite unusual. In the bulk, small deviations from the 3+ valence usually occur in Ce or Yb compounds which show the Kondo effect. This motivated the study of the bulk properties to see, if these small deviations influence the thermodynamic and transport properties of SmRh$_2$Si$_2$.

The crystallographic ThCr$_2$Si$_2$-type structure of SmRh$_2$Si$_2$, figure 1(a), was reported by Felner and Nowik [10, 11] and an isothermal section ($T = 870$ K) of the ternary Sm-Rh-Si phase diagram was explored by Morozkin et al [12, 13]. Susceptibility as well as electrical resistivity measurements on polycrystalline samples were reported by different authors: Signatures of magnetic transitions in the susceptibility at 62, 35 and 10 K and a kink in the resistivity at 60.5 K were observed by Kochetkov et al [14]. Felner and Nowik reported about peaks in the susceptibility at (8 ± 2) K and (46 ± 2) K [11]. These conflicting results in literature, call for a precise determination of the magnetic and thermodynamic properties in high-quality single crystals.
2. Experiment

Single crystals of SmRh$_2$Si$_2$ were grown applying a high-temperature indium-flux method in a Bridgman-type furnace. The high purity starting materials Sm (99.99%, REP), Rh (99.9%, Heraeus), Si (99.999% Wacker), with the molar ratio of 1:2:2, and In (99.9995%, Schuchard) were weighed in a graphite crucible with a volume of 10 ml and sealed in a niobium crucible under argon atmosphere (99.999%). Similar as for the growth of related 122 compounds [15], we used the stoichiometric composition of the elements together with 96 at% In as flux—resulting in a total stoichiometry of 1:2:24 (Sm: Rh: Si: In). The filled Nb-crucible was put under a stream of Ar in a resistive furnace (GERO HTRV 70-250/18) where it was heated up to 1550 °C. A more detailed description of the setup can be found in [16]. The melt was homogenized for one hour and then cooled by slow moving the whole furnace with 1 mm h$^{-1}$ which lead to a cooling rate of 0.5–4 K h$^{-1}$. SmRh$_2$Si$_2$ melts incongruently at approximately 1760 °C[17]. The flux-growth technique enables us to grow crystals at temperatures far below the high melting points of the elements (Sm 1072 °C, Rh 1964 °C, and Si 1414 °C). We optimized our crystal growth procedure with respect to the temperature-time profile without changing the stoichiometry of the educts or the material-to-flux ratio. We found that the best result was obtained when heating up to 1550 °C for a homogenization step of one hour and afterwards starting a slow cooling at 1520 °C with a total time of 90 hours. At the end of this step, the temperature was 1270 °C. Afterwards the crucible was cooled down to room temperature with 200 K h$^{-1}$. Starting the slow cooling at 1520 °C yielded larger crystals compared to a run where the slow cooling was started at 1500 °C. In experiments where the slow cooling was extended over (120 h) 160 h with a final temperature of (1000 °C) 1050 °C we observed the growth of a thin layer of a Rh-Si side phase on top of the SmRh$_2$Si$_2$ single crystals. After cooling, the excess In was removed by etching with hydrochloric acid. Typical single crystals as the one shown in figure 1(c) have a platelet habit with the shortest dimension, 100–400 μm, along the crystallographic c-direction and 1–2 mm perpendicular to that direction. Few single crystals had an extension in c-direction of about 1 mm and thus were suitable for transport measurements along this direction.

The chemical composition determined by energy-dispersive x-ray spectroscopy (EDX) revealed (20 ± 1) at% Sm, (40 ± 1) at% Rh and (40 ± 2) at% Si. We cannot exclude some Rh-Si site exchange within these error bars which is a common problem in this structure type. From a detailed structural and chemical analysis which was performed on the related compound YbRh$_2$Si$_2$ by highly accurate x-ray diffraction and wavelength dispersive x-ray spectroscopy [18] it is known that the structure accepts some Rh-Si site exchange, with a rather small homogeneity range for Rh of 40.0–40.2 at%. The crystal structure was characterized by powder x-ray diffraction (PXRD) on crushed single crystals, using Cu-K$_\alpha$ radiation. PXRD confirmed the I4/mmm tetragonal structure with lattice parameters a = 4.0555(2) Å and c = 10.040(2)(4) Å, which is in agreement with the data published for polycrystalline samples [10]. The orientation of the single crystals was determined using a Laue camera with x-ray radiation from a tungsten anode. The sharp reflexes in the Laue pattern, figure 1(b), demonstrate the high quality of the single crystals. The single crystals grow as platelets with the c-direction.
perpendicular to their surface. Four-point resistivity, magnetization, and heat-capacity measurements were performed using the measurement options of a Quantum Design Physical Properties Measurement System.

3. Results and discussion

3.1. Heat capacity and entropy

In figure 2 (a), the temperature dependence of the specific heat is shown for the two related materials SmRh$_2$Si$_2$ and LuRh$_2$Si$_2$ [19]. LuRh$_2$Si$_2$ with its completely filled 4f-shell is a non-magnetic reference system. The specific heat of SmRh$_2$Si$_2$ shows a pronounced and sharp $\lambda$-type anomaly at $T_N = 64$ K, which establishes a second order phase transition into the antiferromagnetically (AFM) ordered phase. Inset (b) in figure 2 displays $C/T$ versus $T^2$. Between 20 K$^2 < T^2 < 60$ K$^2$, $C/T$ of SmRh$_2$Si$_2$ is nearly equal to $C/T$ of LuRh$_2$Si$_2$, which shows that magnetic excitations are frozen out indicating the presence of a gap in the magnon spectra. Above $T^2 = 60$ K$^2$, $C/T$ of SmRh$_2$Si$_2$ increases much stronger than $C/T$ of LuRh$_2$Si$_2$ which exhibits a nearly linear behavior. This much stronger increase corresponds to the exponential thermal activation of magnetic excitations across the gap. This gap very likely results from the magnetic anisotropy not only between the c and the in-plane direction, but also within the plane as evidenced by magnetization data (see below discussion of figure 4). While both LuRh$_2$Si$_2$ and LaRh$_2$Si$_2$ show a linear behavior in $C/T(T)$ versus $T^2$ for $T^2 < 60$ K$^2$, SmRh$_2$Si$_2$ still present a small positive curvature resulting in slightly larger values of $C/T$ than in LuRh$_2$Si$_2$ at lowest $T$. This indicate the onset of an additional contribution to $C/T$ at lowest $T$, which is likely connected with the nuclear contribution, but might also origin from magnetic defects. The presence of this additional low $T$ contribution prevents a direct determination of the Sommerfeld coefficient $\gamma_0$ and of the low $T$ Debye temperature $\Theta_D$. However, the observation that for $T^2 < 80$ K$^2$ SmRh$_2$Si$_2$ presents nearly the same $C/T$ as LuRh$_2$Si$_2$ indicate that $\gamma_0$ and $\Theta_D$ of SmRh$_2$Si$_2$ are very close to those of LuRh$_2$Si$_2$, $\gamma_0 \approx 7$ mJ/(molK$^2$) and $\Theta_D = 380$ K.

By subtracting the heat capacity of the non-magnetic reference compound LuRh$_2$Si$_2$ [19] we obtained the magnetic part of the specific heat $C^{\text{m}}$ and by integrating $C^{\text{m}}/T$ the entropy $S^{\text{m}}$. Figure 2 inset (c) shows that $S^{\text{m}}$ increases up to the phase transition and increases further towards higher temperature. The Sm ion with $J = 5/2$ has 6 possible states and the entropy of the full crystalline electric field (CEF) multiplet would amount to $S^{\text{m}} = R \ln 6$ at the phase transition. We find that the entropy is strongly influenced by the CEF. It is smaller than $R \ln 6$ and larger than $R \ln 2$ at the phase transition which shows that besides the ground state doublet also the occupation of higher levels contributes to the entropy.

Electrical resistivity

Electrical transport data shown in figure 1, indicate an anisotropic behaviour for current flowing parallel and perpendicular to the [001]-direction below $T_N$. We determined $RR_{1.8 K}^\parallel \parallel = (\rho(300 \text{ K})/\rho(1.8 \text{ K}))^{\parallel \parallel} = 10$ and $RR_{1.8 K}^{\parallel \perp} = 25$. The absolute value of $\rho(T)$ at room temperature for the in-plane resistivity was about 80 $\mu\Omega$cm.
For better comparison of the data with \( j \parallel c \) and \( j \perp c \), we present the normalized resistivity \( T_{300K} r(T) \). For both directions, the resistivity shows a quasi-linear-in-\( T \) behaviour from 300 K to the AFM phase transition. Upon cooling, at \( T_N \) a change of the slope of the resistivity curves occurs and the decrease of the resistivity becomes stronger. In previous work, \( \rho_{200K}/\rho_0 \sim 5 \) was determined for polycrystalline material \[14\]. The residual resistivity ratios \( RRR = \rho_{300K}/\rho_0 \sim 25 \) (corresponding to \( \rho_{200K}/\rho_0 \sim 17.5 \)) determined on our samples for \( j \perp c \) shows that we succeeded in growing high-quality crystals using the indium-flux method.

### 3.2. Magnetization

The magnetic moment of the Sm ions in SmRh\(_2\)Si\(_2\) is small and great care needs to be taken to subtract the background contribution. We therefore studied this material by using large single crystals with a mass of about 30 mg. In figure 3, the temperature dependence of the susceptibility for a field of \( B = 5 \) T along two main symmetry directions is shown. Upon cooling, the transition into the AFM-ordered state appears at the Néel temperature \( T_N = 65 \) K. For \( B \perp c \), the susceptibility decreases strongly below \( T_N \) and shows a small increase at lowest temperatures. This feature varies from sample to sample and is probably caused by a paramagnetic defect contribution. The comparison of the susceptibility curves for both field directions suggests that below \( T_N \) the magnetic moments are ordered within the basal plane of the tetragonal lattice. Additionally, our data shows the absence of further magnetic transitions which were proposed by \[10\] and \[14\] in previous works. Above \( T_N \), the \( T \) dependence of the susceptibility is typical for a \( \text{Sm}^{3+} \) system, cf figure 3. It first shows in a small \( T \) range a Curie-Weiss like decrease, then evolves towards a large \( T \) independent susceptibility, and for field along the \( c \) axis even show a slight increase towards higher temperatures. This peculiar \( T \) dependence which significantly differs from the Curie-Weiss behaviour observed for most other rare earth can easily be accounted for by the specific properties of the 4f state of \( \text{Sm}^{3+} \). In the \( f = L - S = 5/2 \) ground state multiplet of the 4f\(^5\) state of \( \text{Sm}^{3+} \) the almost cancellation of the orbital part of the moment with \( L = 5 \), \( g_{\text{orb}} = 1 \) by the spin part with \( S = 5/2 \), \( g_{\text{spi}} = 2 \) results in a tiny Landé factor \( g_L = 0.286 \). This leads to a quite small value of the effective moment, \( \mu_{\text{eff}} = 0.84 \mu_B \) and, accordingly, to a small Curie-Weiss contribution. In contrast, the first excited multiplet

![Figure 3. SmRh\(_2\)Si\(_2\). Top: Susceptibility \( \chi(T) \) as a function of temperature for \( B \parallel 001 \) and \( B \perp 001 \). The susceptibility was calculated using the standard expression including Curie and Van-Vleck contributions and with the first excited \( f = 7/2 \) multiplet set at 1500 K (grey dots). Bottom: Because of the dominant \( T \)-independent Van-Vleck contributions, a tendency towards a Curie-Weiss behaviour in the inverse susceptibility is only seen at low temperatures, just above \( T_N \). The inverse susceptibility \( \chi^{-1}(T) \) does not show Curie-Weiss behaviour at high temperatures.](image-url)
$J = 7/2$ being at a comparatively low energy $E_{7/2} \approx 1500$ K [21] results in a large $T$-independent Van-Vleck type susceptibility which overwhelms the Curie contribution at $T > 200$ K. Further on the increase of the susceptibility for $T > 400$ K is due to thermal excitation of the $J = 7/2$ multiplet, because it has a much larger Landé factor $g_L = 0.825$, and thus a much larger effective moment $\mu_{\text{eff}} = 3.28 \mu_B$. Therefore the prefactor of its Curie contribution is a factor of 15 larger than that of the $J = 5/2$ ground state multiplet. The further excited $J$ multiplets enhance this behaviour. The observed susceptibility, cf figure 3, qualitatively agrees with that calculated for an isolated Sm$^{3+}$ ion using the standard expression for Sm$^{3+}$ and Eu$^{3+}$ systems, see e.g. [22] (figure 3, grey dots), but presents a number of differences, e.g. a clear anisotropy. This anisotropy is likely dominated by the effect of the crystal electric field which affects both, the Curie contribution of the different multiplet states as well as the Van-Vleck contribution. But especially at low temperatures it is also affected by the exchange interaction, which also seems to be anisotropic. Due to the low susceptibility of the Sm$^{3+}$ ions, contributions of the conduction electrons namely Pauli, orbital and diamagnetic susceptibility need to be taken into account. At high temperatures, the difference between the calculated curve (grey dots) and the measured susceptibility is about $2.0 \cdot 10^{-9}$ m$^3$/mol. This is in perfect agreement with the susceptibility of the non-4f electrons determined for LaRh$_2$Si$_2$ by [23]. The field dependence of the magnetization was investigated at $T = 2.15$ K in fields up to $B = 9$ T. In the upper panel of figure 4, the magnetization for fields applied along the main symmetry directions is shown. Here, the magnetization shows anisotropic hysteresis effects. While the slope of $M$ is nearly constant for field $B$ along the [001] direction, red curve in figure 4, for $B \perp$ 001, it is smaller and shows hysteresis effects, black and blue curves. This field dependent behaviour is consistent with a moment orientation in the basal plane of the tetragonal lattice. The occurrence and size of the hysteresis effects is strongly sample dependent and does not resemble the behaviour of a ferromagnetic impurity phase. We speculate that these sample dependent effects might be caused by a tiny amount of included indium flux or Rh-Si side phases. Small flux inclusions are not directly detectable in magnetization or transport measurements but might act as pinning centers for the magnetic domains in this material.
4. Summary

We have grown SmRh$_2$Si$_2$ single crystals for the first time by a high-temperature indium-flux method in a Bridgman-type furnace which enables us not only to determine precisely the phase transition temperature but also to study the anisotropic behaviour of this compound via electrical transport and magnetization measurements. After an optimization of the temperature-time profile of the growth experiment, we obtained millimetre-sized single crystals in the space group I4 /mmm with a platelet habit with the c axis perpendicular to the platelet. The specific heat of SmRh$_2$Si$_2$ shows only one sharp $\lambda$-type anomaly at $T_N = 64$ K, establishing a second order phase transition into the AFM ordered phase. Magnetic measurements on the single crystals show the ordering of the Sm$^{3+}$ moments at $T_N$ as well as the reorientation of magnetic domains for an external field applied in the basal plane of the tetragonal lattice. Above $T_N$, the susceptibility presents the typical behavior of a Sm$^{3+}$ system. It shows a small Curie-Weiss contribution below 100 K due to the tiny Landé factor of the $J = 5/2$ ground state multiplet, but a large $T$-independent Van-Vleck contribution which dominates the susceptibility above 200 K and results from low lying excited $J$ multiplets of Sm$^{3+}$. Below $T_N$, electrical transport data show an anisotropy between the resistivity measured with current parallel and perpendicular to the c axis. The residual resistivity ratio RRR $= \rho_{300K}/\rho_0 \sim 25$ indicates that we succeeded in growing high-quality single crystals from a high-temperature indium flux. Previous ARPES studies [6] hint to a possible Kondo screening of the Sm$^{3+}$ ions but we could not detect any effect in the transport and thermodynamic properties.

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