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Crystal growth by Bridgman and Czochralski method of the ferromagnetic quantum critical material $YbNi_4P_2$

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ABSTRACT

The tetragonal $YbNi_4P_2$ is one of the rare examples of compounds that allow the investigation of a ferromagnetic quantum critical point. We report in detail on two different methods which have been used to grow $YbNi_4P_2$ single crystals from a self-flux. The first, a modified Bridgman method, using a closed crucible system yields needle-shaped single crystals oriented along the [001]-direction. The second method, the Czochralski growth from a levitating melt, yields large single crystals which can be cut in any desired orientation. With this crucible-free method, samples without flux inclusions and a resistivity ratio at 1.8 K of $RR_{1.8\,K} = 17$ have been grown.

1. Introduction

In the last decades, compounds containing lanthanides (Ln) have been studied due to their large variety of interesting physical properties like quantum criticality, intermediate valence states, complex or anisotropic magnetism, heavy fermion behavior as well as the occurence of unconventional superconductivity [1–4]. Growing crystals of Yb compounds containing transition metals means dealing with the high vapor pressure of the first and the high melting temperature of the latter. For the crystal growth therefore often a flux method at high temperatures is applied. By using a flux it is possible to solve the high-melting elements as well as the elements with low boiling points and obtain a melt with a moderate vapor pressure which is suitable for the growth. A good overview about the use of metallic fluxes is given in [5,6]. In the past, the flux method has been successfully applied for the growth of Ln compounds using indium, tin or lithium as flux [7–12]. In some cases, the use of a solvent leads to the formation of unwanted phases, in this regard the use of a self-flux can be more successful. Even when using a flux, the growth temperature often exceeds 1200 °C. Due to the highly volatile and reactive constituents the growth usually is performed in a closed Nb or Ta crucible. Another attempt is the application of inert gas pressure during the growth. Due to its high reactivity, reports on the growth of phosphorous containing bulk single crystals are rare. Binary phosphides have been grown by a liquid-encapsulated Czochralski method (InP [13,14]), by chemical vapor phase transport (CuP_2 [15]) or under high pressure (CoP_3 [16]). Ternary phosphides have been grown in a closed crucible from tin flux ($LnRu_2P_2$ [17,11]) or by applying the ACRT Bridgman method ($ZnGeP_2$ [18]).

Within this manuscript, we report in detail on the growth of the intermetallic compound $YbNi_4P_2$. Quantum phase transitions that occur at zero temperature are of current interest in solid state physics. $YbNi_4P_2$ is one of the rare examples of compounds that allow the investigation of a ferromagnetic quantum critical point (FM QCP). Low-temperature measurements of Steppke et al. [19] indicate the existence of a FM QCP in $YbNi_4(P_{1-x}As_x)_2$. For further investigation of this intriguing phenomenon, high quality as well as large single crystals are essential. $YbNi_4P_2$ crystallizes in the tetragonal $ZrFe_4Si_2$ structure type ($P4_2/mnm$). In this rather unexplored structure type, the Yb atoms are located in channels of Ni tetrahedral chains leading to quasi-1D character also of the electronic structure of this compound. $YbNi_4P_2$ is a heavy fermion compound ($T_K \approx 8$ K) and orders ferromagnetically below $T_C \approx 150$ mK [20]. The magnetic properties were investigated by magnetization measurements [21,22,20,23], NMR [24,25] and μSR [26]. Inelastic neutron scattering on powder was performed to investigate the crystalline electric-field splitting and ferromagnetic fluctuations [27,28].

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2. Experimental details

High-purity starting materials Yb ingot (99.9%, Strem Chemicals), Ni slugs (99.995%, Alfa Aesar), red P pieces (99.999%, Mining & Chemical Products Ltd.) were used. Some of the reagents, namely ytterbium and phosphorous, are air sensitive. The preparation of these reagents was done in a glove box filled with purified argon. The stoichiometric composition of the elements was weighed in together with 50 at% $Ni_{81}P_{19}$ (eutectic composition) as flux resulting in a sample to flux ratio of 1:1. The total mass of each growth charge was 15 g. The elements were filled in a graphite crucible ($V=25$ ml) for the Bridgman growth and in a boron nitride crucible ($V=30$ ml) for the preparation of the precursor for the Czochralski growth. The inner crucible was put in an outer crucible made of tantalum which was sealed under Ar using arc-melting. Differential thermal analysis was done using a Simultaneous Thermal Analysis device (STA 449 C, Netzsch), which allows simultaneous thermogravimetry (TG) and differential thermal analysis (DTA). For the Bridgman growth, the Ta-crucible was put under a stream of Ar in a vertical resistive furnace (GERO HTRV70–250/18) in which a maximum temperature of 1350 °C was used in our experiment. During the growth, the temperature was measured in situ at the bottom of the tantalum crucible by a thermocouple of type B. After the Bridgman growth, the excess flux was spun of in a centrifuge (Christ UJ1) at ≈1100°C. The Czochralski growth experiment was performed in a commercial ADL (Arthur D. Little) high-frequency growth device equipped with a generator that provides a maximum power of about 30 kW. The temperature was measured with an IRCON pyrometer. The crystal structure was characterized by powder X-ray diffraction on crushed single crystals, using $Cu - K_\alpha$ radiation.The chemical composition was measured by energy-dispersive X-ray spectroscopy (EDX). The orientation of the single crystals was determined using a Laue camera with X-ray radiation from a tungsten anode. Four-point resistivity and magnetization measurements were performed using the commercial measurement options of a Quantum Design PPMS.

3. Crystal growth

A complete ternary phase diagram of Yb–Ni–P compounds at high temperatures does not exist, but an isothermal section ($T=870$ K) of this phase diagram was determined by Kuz'ma et al. [29]. Several stable ternary phases exist in the vicinity of $YbNi_4P_2$. In previous work, the decomposition of $YbNi_4P_2$ above 1500 °C at ambient pressure was observed [20]. Therefore, one expects that the crystal growth of the stoichiometric compound by floating-zone or the Czochralski method not to be successful. The binary Ni–P phase diagram shows a low-melting eutectic, $Ni_{81}P_{19}$ [30]. A detailed investigation identified $Ni_{80.4}P_{19.6}$ as the eutectic composition with the eutectic temperature $T_E = 875$ °C [31]. We have used this eutectic as a self-flux in one series of experiments utilizing a Bridgman and in an other series the Czochralski technique to grow $YbNi_4P_2$ single crystals. One further problem is that the Yb–Ni–P melt exhibits a high reactivity with other materials leading to lack of inert crucible material. For the determination of the crystallization temperature of $YbNi_4P_2$ in $Ni_{81}P_{19}$ simultaneous TG and DTA have been performed before starting the growth experiments. 555 mg of prereacted material consisting of 50 at% $YbNi_4P_2$ and 50 at% $Ni_{81}P_{19}$ was put in an open alumina crucible and heated with 10 K/min in an Ar stream. The weight loss after 3 heat/cool cycles was $\Delta m/m \approx 0.05$ and the signals of all three runs were reproducible. The DTA curve presented in Fig. 1 shows the third cooling process. During heating, the melting signal of the eutectic shows up at 870 °C. The melting signal of the 142-

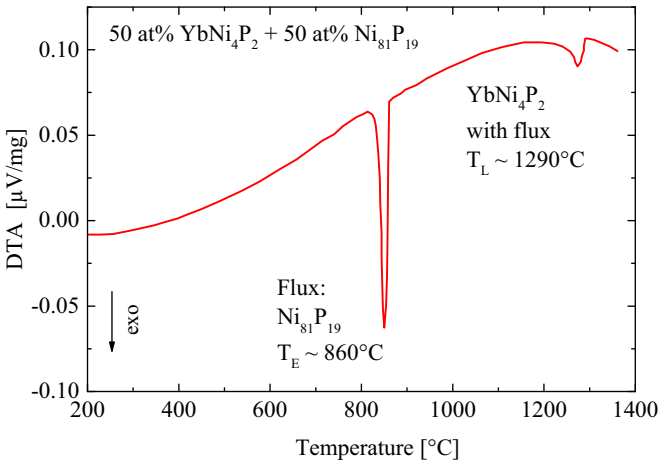

Fig. 1. The DTA signal recorded during cooling shows a dip at the liquidus temperature of the starting charge $T_L \approx 1290$ °C marking the onset of the crystallization of $YbNi_4P_2$. A second dip occurs at the eutectic temperature $T_E \approx 860$ °C.

compound is located at ≈1340 °C and relatively weak. The high melting temperature of the transition metal Ni(1455 °C) in combination with the starting sublimation of red P at low temperature (416 °C) and its high reactivity additionally to the low boiling point (1196 °C) and high vapor pressure of Yb necessitates the preparation of a precursor.

3.1. Bridgman method

$YbNi_4P_2$ single crystals were grown by a modified Bridgman method from a Ni–P self-flux for the first time in 2012 [23]. In the mean time, the growth procedure has been optimized and several physical properties of this compound have been investigated, but a detailed description of the growth parameters has not been reported yet. For the Bridgman growth, the sealed Ta-crucible was slowly heated up to 700°C with a rate of 30 K/h to allow a slow reaction of phosphorous with the other elements and to 1350°C with a rate of 50 K/h. The melt was held at this temperature for 1 h to ensure homogenization and then cooled by slow moving of the whole furnace with 0.88–3.4 mm/h leading to a cooling rate in the range of 0.5–4 K/h down to 1000 °C, while the position of the crucible stayed fixed. With this setup, we are able to cool the sample without vibrations resulting from the movement which is different from the conventional Bridgman process where the sample is moved from the hotter to the cooler zone. After the growth, the $YbNi_4P_2$ single crystals are embedded in the Ni-Ni_3P eutectic. A typical growth result (cut image) with the $YbNi_4P_2$ single crystals embedded in the flux is shown in Fig. 2. Since the flux can not be removed by acids without solving the crystals, the use of a centrifuge was necessary to separate the crystals from the flux. In preparation of the centrifugation process, the sample was cut using a spark erosion device and placed above some glassy carbon pieces and a graphite sieve in a fused silica ampoule. The ampoule was heated in a box furnace up to 1100 °C, held at this temperature for one hour and then within a few seconds moved into a centrifuge. The flux with the eutectic temperature of ≈870°C was spun of. Afterwards, the remaining crystals could be easily separated from each other manually. The long, rod shaped single crystals are presented in Fig. 3.

3.2. Czochralski growth from a levitating melt

In the past, the successful single crystal growth of cerium compounds in the same high frequency furnace that we used has been reported [32–34]. $YbNi_4P_2$ single crystals were grown from a