Single crystal growth of the ErPd$_2$Si$_2$ intermetallic compound

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Bulk single crystals of ErPd$_2$Si$_2$, with ThCr$_2$Si$_2$-type body-centered tetragonal structure have been successfully grown under a purified Ar atmosphere at a velocity of 10 mm/h using a floating zone method with optical radiation heating. The preferred crystal growth direction is close to the [110] orientation with an inclination angle of 15° against the rod axis. The as-grown crystals are Pd-depleted with respect to their nominal stoichiometry ErPd$_2$Si$_2$. The crystals contain small Er-oxide particles. The single-crystalline specimen shows antiferromagnetic ordering indicated by a λ-type singularity of the specific heat capacity $c_p(T)$ at $T_N = 3.4$ K. A broad anomaly around 15–20 K in the magnetic contribution to $c_p(T)$ indicates two-level Schottky-type behavior similar to that of PrPd$_2$Si$_2$.

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1. Introduction

Because of their variety of low temperature physical properties, such as complex magnetic ordering, valence fluctuation, Kondo effect, superconducting, heavy fermion and non-Fermi-liquid behavior RT$_2$Si$_2$ (R=rare earth, T=transition metal) ternary intermetallic compounds crystallizing in the ThCr$_2$Si$_2$-type body-centered tetragonal structure (space group I4/mmm) are a subject of intensive studies$^{[1,2]}$. The magnetization and magnetic structures of polycrystalline ErPd$_2$Si$_2$ have been investigated during past decades, but the results were not unambiguous. Magnetic susceptibility measurement did not reveal any clear magnetic ordering down to 4.2 K$^{[3]}$. Bazela et al.$^{[4]}$ performed neutron diffraction measurements and found magnetic ordering at 2 K with a sine-modulated structure. The bulk magnetization, Mössbauer and neutron diffraction measurements by Tomala et al.$^{[5]}$ show that the compound orders antiferromagnetically below 4.8 K with complex modulated magnetic structures where Er magnetic moments are aligned along the c-axis.

Large single crystals are mandatory for determination of the intrinsic anisotropic structural and physical properties. So far no information is available on the single crystal growth of ErPd$_2$Si$_2$. In a previous paper ternary Er-Pd-Si phase diagram sections have been evaluated with regard to the crystallization of Er$_2$PdSi$_3$ and ErPd$_2$Si$_2$ intermetallic compounds$^{[6]}$, which provide a sound basis for crystal growth. The compound ErPd$_2$Si$_2$ displays a wide homogeneity range (19–22 at% Er, 32–36 at% Pd, 40–46 at% Si) and melts congruently at about 1420 °C$^{[6]}$. A special challenge of crystal growth is the high reactivity of the melt containing the rare earth constituent Er, which favors the application of a floating zone (FZ) method.

The present work is focused on the growth of ErPd$_2$Si$_2$ single crystals by a vertical floating zone technique with optical radiation heating. Large rod shaped single crystals with high quality have been obtained.

2. Experimental procedure

The Er–Pd–Si master alloys have been prepared in a two-step melting process. Pd (99.95% purity) and Si (99.9999% purity) were melted in an arc-melting furnace under a Zr-gettered Ar atmosphere. The arc-melted Pd–Si button together with Er (99.98%) was co-melted in a Hukin-type RF cold-crucible equipment and the levitated melt was cast into a copper mold to form a polycrystalline feed rod, 6 mm in diameter and 60 mm in length. Different feed rod compositions with minor deviations from the nominal stoichiometry Er$_{20}$Pd$_{40}$Si$_{40}$ were used for crystal growth. The ErPd$_2$Si$_2$ single crystal was grown by an FZ technique with optical radiation heating$^{[7]}$. The growth process proceeds in a vacuum chamber under 0.12 MPa flowing Ar purified by a Ti-getter system at the gas inlet$^{[8]}$. Axially symmetric counter-rotation of the crystal (33 rpm) and feed rod (20 rpm) was applied to grow...
ErPd₂Si₂ single crystals of about 6 mm in diameter and 40 mm in length. The orientation of single crystals was determined by the X-ray Laue back-scattering method. Microstructure and crystal perfection were examined by metallography using optical polarized-light microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) in the energy dispersive X-ray (EDX) mode. The specific heat was measured by means of a Quantum Design PPMS using a relaxation method.

3. Results and discussion

FZ experiments with a variety of feed rod compositions and process parameters were accomplished. During the crystal growth process the shape of the FZ and its temperature were continuously controlled by a video device and a two-color pyrometer (using a stroboscopic method), respectively [9]. Because of the constituent Er the melt is very sensitive to oxidation. Only the middle part of the floating zone displayed a shiny surface. Otherwise it is covered by oxides, which form a dense oxygen scale adjacent to the melting feed rod. By evaporation from the melt the quartz walls of the growth chamber are covered with opaque deposits, which lead to light absorption balanced by an increasing power supply during the growth process. After certain time intervals, axial temperature profiles across the floating zone surface were recorded which exhibit a narrow plateau at 1430 °C just above the melting temperature (1420 °C). The temperature falls sharply towards both sides, with a steep temperature gradient of ≈ 35 K/mm at the growth interface. However, because of the oxygen scale and the likely light absorption at the container walls the absolute temperatures are largely uncertain.

A comparatively fast growth velocity of 10 mm/s was chosen because ErPd₂Si₂ is a congruently melting compound [6]. A photo of the as-grown crystal together with the feed rod and quenched last zone is shown in Fig. 1a. The growth direction and the principal crystallographic axes are marked by arrows. The orientation with respect to the rod axis has been determined at the crystal cross section from the X-ray Laue back-scattering diffraction pattern (Fig. 1b). The growth direction is close to the crystalographic orientation [110] in the plane perpendicular to the c-axis of the tetragonal unit cell (inclination 15°).

The grain selection at the beginning of the crystal growth process is illustrated in Fig. 2a by a longitudinal section parallel to the rod axis. Here, a seed with coarse columnar grains from a former growth trial and a feed rod with Pd-lean composition Er₂Pd₃₆.₅Si₄₀.₅ were used. Under these circumstances the grain selection ensues within about 5 mm without precipitation of any secondary phase. It is apparent, that the coarse-crystalline rod is susceptible to crack formation because of the anisotropic thermal contraction during the cooling process. Finally, the whole cross section is covered by a single grain as demonstrated in Fig. 2b. The perfection of crystal matrix suffers from homogeneously distributed oxide inclusions (basically Er₂O₃). The irregular shape of oxide particles revealed by SEM suggests that they originate from debris caused by melt oxidation but not from precipitation during cooling. The EPMA of the ErPd₂Si₂ single crystal disclosed a Pd-lean composition, 21.8 ± 0.5 at% Er, 36.8 ± 0.5 at% Pd, and 41.4 ± 0.5 at% Si, in comparison to the nominal stoichiometry that correlates with the feed rod utilized. The lattice parameters, a=4.104(2) Å and c=9.878(6) Å, determined from powder diffraction X-ray analysis of a ground crystal slice match with the homogeneity range of the ErPd₂Si₂ compound previously determined for a series of ErPd₂(2−x)Si(2−x) polycrystalline specimens [6].

The investigation of the quenched floating zone can deliver valuable information on the crystallization process and its optimization. The longitudinal sections through the last part of the crystal and the quenched zone, shown in Fig. 3, proved the slightly convex shape of the growth front towards the melt (Fig. 3a). This is an important point for efficient grain selection during crystal growth. Small volume fractions of the Er₂Pd₃Si₃ secondary phase...
We found out that the type of minority phases arising in the quenched ultimate zone depends on feed rod composition.

The physical properties of the ErPd$_2$Si$_2$ crystal were studied with regard to the expected low temperature magnetic ordering. The specific heat capacity was measured in a temperature interval 1.8 K < T < 50 K.

The onset of long range antiferromagnetic order is signaled by a sharp anomaly in the specific heat of the ErPd$_2$Si$_2$ crystal at $T_N \approx 3.4$ K (Fig. 4), which coincides with the steepest slope of the magnetic susceptibility $\chi(T)$ [10]. Magnetic ordering in ErPd$_2$Si$_2$ is more complex than that deduced from polycrystalline specimens in the past; details have been published elsewhere [10]. A significant anisotropy has been detected in magnetization with the [001] crystallographic direction being the magnetic easy axis, in agreement with neutron data [5]. The magnetic susceptibility indicates antiferromagnetic correlations well above $T_N$ as also deduced from previously reported slow-relaxation dominated Mössbauer spectra [5]. In order to obtain the magnetic contribution to the specific heat $c_{\text{magn}}$ of ErPd$_2$Si$_2$, the specific heat of the isomorphous non-magnetic analog LaPd$_2$Si$_2$ (from Ref. [11]) has been subtracted from the data (compare also Ref. [12]). Note, that the reference data have been scaled by $(m/\bar{m})^{1/2}$, where $m$ and $\bar{m}$ are the molar masses of ErPd$_2$Si$_2$ and LaPd$_2$Si$_2$, respectively, in order to account for the different masses of La and Er. The resulting magnetic contribution to the specific heat indeed indicates significant magnetic entropy changes above $T_N$. A prominent feature is a broad hump in $c_{\text{magn}}(T)$ around 15–20 K, which is also seen in $\chi(T)$ for $H||[110]$. The broad anomaly indicates a two-level Schottky-type behavior, which can be associated with temperature-driven population of crystal-field (CF) split states. The maximum of the Schottky-anomaly suggests level splitting $\Delta \approx 50$ K, similar to PrPd$_2$Si$_2$ [13], and a degeneracy ratio of the associated states of $g_{\text{Er}}/g_{\text{La}} = 1.4$. Our data $T \sim 2$ K allow only rough estimates on the entropy changes at low temperature. Extrapolating the data by a $T^2$-behavior may suggest a non-degenerated lowest doublet CF state. The electrical conductivity of ErPd$_2$Si$_2$ single crystals exhibits neither noteworthy anisotropy nor anomalies related to the magnetic transition temperatures [10].

4. Summary and conclusions

Bulk single crystals of the ErPd$_2$Si$_2$ compound have been successfully grown under purified Ar atmosphere at a velocity of 10 mm/h using an FZ method with optical radiation heating. The X-ray Laue back-scattering analysis indicates a preferred crystal growth direction close to $[110]$ orientation. The as-grown crystals are Pd-depleted with respect to the nominal stoichiometry of ErPd$_2$Si$_2$. The highly reactive Er–Pd–Si melt leads to partial oxidation of the FZ surface and Er-oxide inclusions degrading the crystal perfection. The single-crystalline specimen shows antiferromagnetic ordering indicated by a $\lambda$-type singularity of the specific heat capacity at $T_N = 3.4$ K. A broad anomaly around 15–20 K in the magnetic contribution to the specific heat is attributed to a two-level Schottky-type behavior. The single crystals present considerable anisotropy of the complex magnetic ordering behavior and the existence of magnetic fluctuations above $T_N$.

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