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Single crystal growth of the $ErPd_2Si_2$ intermetallic compound

Chongde Cao [a,b,c,*], Rüdiger Klingeler [d], Norman Leps [b], Günter Behr [b], Wolfgang Löser [b]

[a] Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, PR China
[b] Leibniz-Institut für Festkörper- und Werkstoffforschung (IFW) Dresden, Postfach 270116, D-01171 Dresden, Germany
[c] State Key Laboratory of Solidification of China, School of Materials Science and Engineering, Xi'an 710072, PR China
[d] Kirchhoff Institute for Physics, Heidelberg University, D-69120 Heidelberg, Germany

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ABSTRACT

Bulk single crystals of $ErPd_2Si_2$ with $ThCr_2Si_2$-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 $ErPd_2Si_2$. 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 $PrPd_2Si_2$.

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_2Si_2 (R=rare earth, T=transition metal) ternary intermetallic compounds crystallizing in the $ThCr_2Si_2$-type body-centered tetragonal structure (space group I4/mmm) are a subject of intensive studies [1,2]. The magnetization and magnetic structures of polycrystalline $ErPd_2Si_2$ 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 $ErPd_2Si_2$. In a previous paper ternary Er–Pd–Si phase diagram sections have been evaluated with regard to the crystallization of Er_2PdSi_3 and $ErPd_2Si_2$ intermetallic compounds [6], which provide a sound basis for crystal growth. The compound $ErPd_2Si_2$ 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 $ErPd_2Si_2$ 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 $ErPd_2Si_2$ 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

* Corresponding author at: Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, PR China. Tel.: +86 29 88431657; fax: +86 29 88431657.
E-mail address: caocd@nwpu.edu.cn (C. Cao).

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$ErPd_2Si_2$ 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 $ErPd_2Si_2$ 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 crystallographic orientation [110] in the plane perpendicular to the *c*-axis of the tetragonal unit cell (inclination 15°).

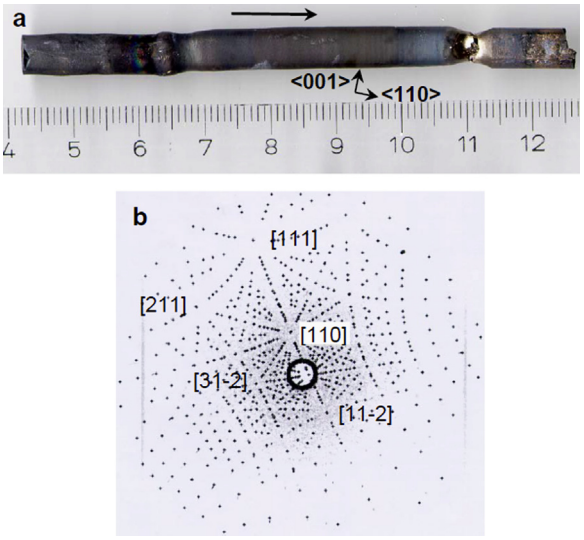

Fig. 1. (a) Single crystal of $ErPd_2Si_2$ grown by the FZ technique with optical heating. The growth direction is marked by an arrow and the inclination of the rod axis with respect to the crystallographic orientations [001] and [110] is given. (b) X-ray Laue back-scattering diffraction pattern from the crystal cross section with principal reflections.

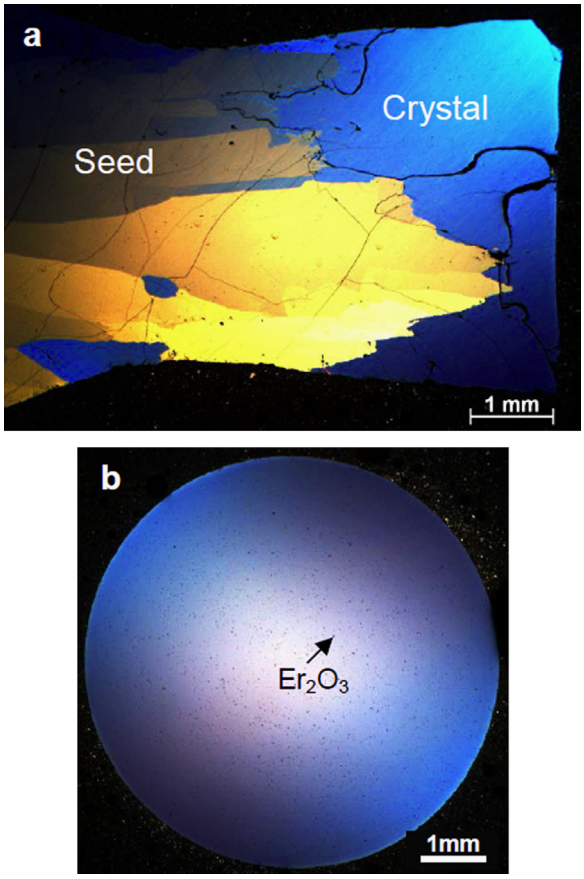

Fig. 2. (a) Optical image of grain selection at the beginning of an $ErPd_2Si_2$ crystal grown from a polycrystalline seed and (b) cross section near end of the FZ growth process showing the complete single crystalline nature of the rod and Er_2O_3 defects in the $ErPd_2Si_2$ matrix.

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 $Er_{21}Pd_{38.5}Si_{40.5}$ 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 Er_2O_3). 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 $ErPd_2Si_2$ 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 $ErPd_2Si_2$ compound previously determined for a series of $ErPd_{(2-x)}Si_{(2+x)}$ 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 Er_2PdSi_3 secondary phase

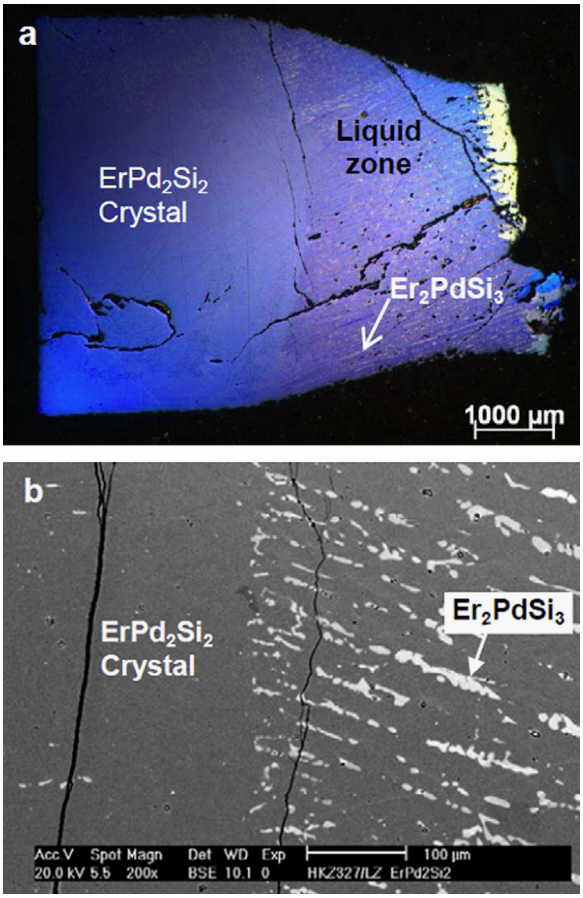

Fig. 3. Longitudinal sections through the final part of the $ErPd_2Si_2$ crystal and the last FZ quenched after growth process: (a) optical image illustrating the convex interface and (b) SEM image showing the Er_2PdSi_3 minority phase in the quenched FZ.

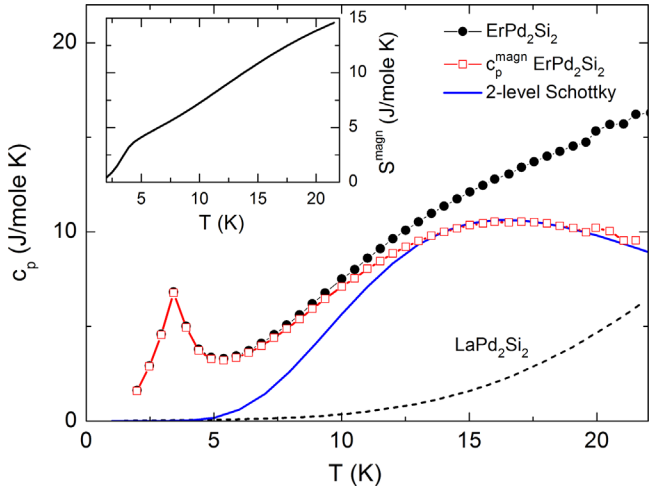

Fig. 4. Specific heat capacity vs. temperature $c_p(T)$ of $ErPd_2Si_2$ single-crystalline specimen (black circles). The dashed line shows the specific heat of $LaPd_2Si_2$ from Ref. [11], red squares label the magnetic specific heat $c_p^{magn}(T)$ of $ErPd_2Si_2$, and the blue solid line displays a degenerated 2-level Schottky-type Approximation with parameters $\Delta = 49.6$ K, and $g_0/g_1 = 0.24$. Inset: magnetic entropy $S^{magn} = \int c_p^{magn}/T\,dT$ vs. temperature. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

(in interdendritic areas) designate a Pd-reduced melt composition in the FZ with regard to the crystal (Fig. 3b). Deviation results from even small differences between the feed rod and crystal composition, which are amplified with the advancing growth process. 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 $ErPd_2Si_2$ crystal were studied with regard to the expected low temperature magnetic ordering. The specific heat capacity was measured in a temperature interval $1.8\ \mathrm{K} < T < 50\ \mathrm{K}$.

The onset of long range antiferromagnetic order is signaled by a sharp anomaly in the specific heat of the $ErPd_2Si_2$ 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 $ErPd_2Si_2$ 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_p^{magn} of $ErPd_2Si_2$, the specific heat of the isomorphic non-magnetic analog $LaPd_2Si_2$ (from Ref. [11]) has been subtracted from the data (compare also Ref. [12]). Note, that the reference data have been scaled by $(m/\tilde{m})^{3/2}$, where m and $\tilde{m}$ are the molar masses of $ErPd_2Si_2$ and $LaPd_2Si_2$, 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 $c_p^{magn}(T)$ 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 $\Delta = 50$ K, similar to $PrPd_2Si_2$ [13], and a degeneracy ratio of the associated states of $g_0/g_1 = 1{:}4$. Our data $T > 2$ K allow only rough estimates on the entropy changes at low temperature. Extrapolating the data by a T^3-behavior may suggest a non-degenerated lowest doublet CF state. The electrical conductivity of $ErPd_2Si_2$ single crystals exhibits neither noteworthy anisotropy nor anomalies related to the magnetic transition temperatures [10].

4. Summary and conclusions

Bulk single crystals of the $ErPd_2Si_2$ 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 $ErPd_2Si_2$. 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 λ-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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