Short Communication

Occurrence of Extinction Correlated with Crystal Growth Mode for Crystals of Pd_3Ce and $MgZn_2$

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In previous single-crystal neutron diffraction analyses of crystals grown at high temperatures it was often observed that the crystals investigated showed strong extinction in the neutron scattering process. This was the case in the investigations of the structures of Ho_2Fe_{17},[1] γ-NbN,[2] and Mo_3Si.[3] To further investigate this problem, single-crystal neutron diffraction measurements have been made on crystals of two compounds grown from the melt: Pd_3Ce, melting point 1437 C,[4] and $MgZn_2$, melting point 588 C.[5] The structures of the two compounds are known. Pd_3Ce has the $CuAu_3$ structure,[6] and $MgZn_2$ is a Laves phase with the C 14 structure.[7] The structures of the two compounds have not been investigated previously by single-crystal neutron diffraction.

The two intermetallic compounds were prepared in a cold crucible in an ADL-MP furnace, starting from 99.95 % Pd (Johnson Matthey), 99.99 % Ce (Rare Earth Products Limited), 99.99 % Mg (Ventron) and 99.99 % Zn (Ventron). An ambient He pressure was used to reduce evaporation from the melts. Single crystals of Pd_3Ce were grown by directional solidification in the cold crucible by slow cooling of the melt, at an ambient He pressure of 1 MPa. Single crystals of $MgZn_2$ were grown in the Bridgman mode from a crucible of BN. The crucible had a conically shaped bottom and was constructed in two parts to facilitate the discharge of the ingot from the crucible. (Fig. 1). The crucible was withdrawn from the heating coil of an ADL-HP furnace at a rate of 3 mm h^{-1}, and the ambient He pressure was 2 MPa.

X-Ray diffraction. The X-ray powder patterns were recorded on a Stoe diffractometer with a position-sensitive detector, using Cu$K\alpha_1$ radiation (λ = 1.54056 Å). The diffractometer was calibrated with $Ag_6Ge_{10}P_{12}$, a = 10.312 Å. From the powder patterns were derived the unit cell parameters reported below.

Neutron diffraction. The four-circle diffractometer at Risø, Denmark, was used in the data collection, using neutrons with λ = 1.007 Å and the ω-2θ scan technique. A single crystal of Pd_3Ce was cut from a slice of the sample made by directional solidification, using spark erosion. The single crystal had the dimensions 2.0×2.0×3.0 mm, and a total of 840 reflections were measured out to $\sin\theta/\lambda = 0.69$. After corrections for absorption ($\mu = 0.211$ cm^{-1}) and data reduction, 25 independent reflections with $I > 3\sigma(I)$ were used in the least-squares refinement with the program LINUS.[8] The scattering lengths were b(Pd) = $0.60 \cdot 10^{-12}$ cm, and b(Ce) = $0.46 \cdot 10^{-12}$ cm.[9] The structure is cubic, a = 4.135 Å. The space group is $Pm3m$ (No. 221), with Pd in 3c (0,0.5,0.5) and Ce in 1a (0,0,0). The structure thus has no variable positional parameters, and only a scale factor and two isotropic temperature factors were refined, yielding U(Pd) = 0.0052(8) and U(Ce) = 0.0064(4) at a conventional R value of 1.6 %. Corrections for extinction did not improve the R value, and the crystal investigated thus shows no extinction within experimental error.

A single crystal of $MgZn_2$ was cut by spark erosion from the sample prepared in the Bridgman growth experiment. The crystal had the dimensions 3.5×2.2×1.8 mm. The unit cell is hexagonal, with $a = b = 5.2234$ and $c = 8.5562$ Å. A total of 2111 reflections were measured out to $\sin\theta/\lambda$ =

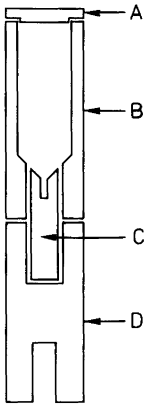

Fig. 1. Sketch of crucible of boron nitride. A: lid; B and C: crucible; D: support of BN. The bottom of the crucible (C) fits tightly to the parts B and D.

Table 1. Positional and thermal parameters for $MgZn_2$; R = 3.0 %.

Atom	Position	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	4*f* ⅓, ⅔, *z* z = 0.0629(2)	0.0133(4)	= U_{11}	0.0119(5)	= ½·U_{11}	0	0
Zn1	2*a* 0, 0, 0	0.0150(5)	= U_{11}	0.0084(6)	= ½·U_{11}	0	0
Zn2	6*h* *x*, 2*x*, ¼ *x* = −0.1697(1)	0.0147(4)	0.0092(4)	0.0133(4)	= ½·U_{22}	0	0

0.81, and after correction for absorption (μ = 0.027 cm^{-1}) and data reduction a total of 198 reflections with $I > 3\sigma(I)$ were used in the structure factor calculations (LINUS). The scattering lengths used were b(Mg) = $0.52 \cdot 10^{-12}$ cm and b(Zn) = $0.57 \cdot 10^{-12}$ cm.[9] The space group is $P6_3/mmc$ (No. 194), with Mg in 4*f*, Zn1 in 2*a* and Zn2 in 6*h*. The parameters refined were a scale factor, two positional parameters and seven anisotropic temperature factor parameters. This gave a conventional R value of 6.8 %. By introducing an isotropic extinction parameter, the R value was reduced to 3.0 %. The final parameters arrived at are listed in Table 1.

The positional parameters found (Table 1) have a higher precision than the parameters reported in Ref. 7, viz. z(Mg) = 0.0630(7), and x(Zn2) = −0.1695(2), which are based on a single-crystal X-ray diffraction measurement.

Of the two crystals investigated, Pd_3Ce, grown at a high temperature (1437 C), showed no extinction and $MgZn_2$, grown at a lower temperature (588 C), showed extinction. Factors of importance for the occurrence of extinction are most likely the growth rate of the crystal and the magnitude of the temperature gradient across the solid-liquid interface, rather than the absolute value of the growth temperature. Pd_3Ce was grown with a small, and $MgZn_2$ with a large temperature gradient across the solid-liquid growth interface.

The three compounds that in previous measurements showed strong extinction were all prepared in different crystal growth modes. Ho_2Fe_{17} was Czochralski-grown from a cold crucible, γ-NbN was grown by solid-state annealing, and Mo_3Si was grown by the travelling-solvent growth method. These growth modes all entail steep temperature gradients across the solid-liquid interface, or the solid-solid interface in the case of γ-NbN.

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