

The Intermetallic Zirconium Compounds ZrNiAl, ZrRhSn, and ZrPtGa – Structural Distortions and Metal-Metal Bonding in Fe₂P Related Compounds

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Z. Naturforsch. **54 b**, 45–53 (1999); received August 20, 1998

Intermetallic Compounds, Crystal Structure, Superstructure, Chemical Bonding

ZrNiAl, ZrPtGa, and ZrRhSn have been prepared by reacting the elements in an arc-melting furnace and subsequent annealing at 970 K. These compounds have previously been investigated only by use of X-ray powder data for ZrPtGa and ZrRhSn and single crystal film data for ZrNiAl. Precise single crystal diffractometer data are reported in the present paper. The structure of ZrNiAl is confirmed. It adopts a substitution variant of the Fe₂P type: $P\bar{6}2m$, $a = 691.5(2)$, $c = 346.6(1)$ pm, $Z = 3$, $wR2 = 0.0538$, 320 F^2 values, 14 parameters. The structure refinement reveals a large displacement parameter U_{33} for one nickel position, indicative of a slight nickel dislocation. Weak superstructure reflections could be found on Guinier powder patterns for ZrPtGa and ZrRhSn. These compounds crystallize with the HfRhSn type structure ($Z = 6$, space group $P\bar{6}2c$), a superstructure of the Fe₂P type: $a = 714.5(1)$, $c = 706.3(2)$ pm, $wR2 = 0.0651$, 594 F^2 values, 18 parameters for ZrPtGa and $a = 734.2(2)$, $c = 721.8(2)$ pm, $wR2 = 0.0349$, 355 F^2 values, 18 parameters for ZrRhSn. Structural motifs of these compounds are transition metal centered trigonal prisms formed by the zirconium, aluminium, gallium, and tin atoms. While these trigonal prisms are regular in ZrNiAl, significant distortions occur in the structures of ZrPtGa and ZrRhSn. Due to the distortions of the trigonal prisms in the superstructures, some platinum and rhodium atoms are dislocated from the subcell mirror planes towards Pt-Pt and Rh-Rh pairs with distances of 310 and 313 pm, respectively. The formation of the superstructure is most likely due to packing reasons. Chemical bonding in ZrRhSn was investigated on the basis of an extended Hückel calculation.

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