

New oxide group-9 transition metal superconductors in the filled-Ti₂Ni type structure

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The Ti₂Ni and the related eta-carbide-type structures are known to exhibit various interesting physical properties. The Ti₂Ni structure is surprisingly complex for an intermetallic structure-type crystallizing in the space group Fd-3m with a unit cell containing of 96 metal atoms [1, 2]. The related eta-carbide-type compounds of the general formula A₄B₂X or A₃B₃X correspond to filled version of the Ti₂Ni structure [2]. The role of the void filling light atom X, which can be carbon, oxygen, or nitrogen, has so far been unclear for the overall physical properties of these materials. Herein, we have successfully synthesized single crystals of Ti₂Co with the Ti₂Ni-type structure and single crystals of eta-carbide-type oxide Ti₄Co₂O. We show that while Ti₂Co is a semiconductor, while its filled-version Ti₄Co₂O is a bulk superconductor with a critical temperature of 2.7 K. We find that the interstitial oxygen plays an crucial role for the overall physical properties. By extending this concept to the other group 9 transition metals, we have successfully synthesized the two new compounds Ti₄Rh₂O and Ti₄Ir₂O. We, furthermore, show that both are new bulk type-II superconductors with superconducting transitions at 2.8 K and 5.3 K, respectively. We present detailed measurements on all three superconductors, showing that all three have remarkably high upper critical field in comparison with their critical temperature. Most noteworthy Ti₄Ir₂O has an upper critical field of 16.06 T, which is exceeding by far the weak-coupling BCS Pauli paramagnetic limit of 9.86 T.

[1] Mackay, Richard, Gordon J. Miller, and Hugo F. Franzen, "New oxides of the filled-Ti₂Ni type structure", *Journal of alloys and compounds* 204.1-2 (1994): 109-118.

[2] Ma, KeYuan, Jorge Lago, and Fabian O. von Rohr, "Superconductivity in the eta-carbide-type oxides Zr₄Rh₂O_x", *Journal of Alloys and Compounds* 796 (2019): 287-292.