

## New oxide group-9 transition metal superconductors in the filled-Ti<sub>2</sub>Ni type structure

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The Ti<sub>2</sub>Ni and the related eta-carbide-type structures are known to exhibit various interesting physical properties. The Ti<sub>2</sub>Ni 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 A<sub>4</sub>B<sub>2</sub>X or A<sub>3</sub>B<sub>3</sub>X correspond to filled version of the Ti<sub>2</sub>Ni 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 Ti<sub>2</sub>Co with the Ti<sub>2</sub>Ni-type structure and single crystals of eta-carbide-type oxide Ti<sub>4</sub>Co<sub>2</sub>O. We show that while Ti<sub>2</sub>Co is a semiconductor, while its filled-version Ti<sub>4</sub>Co<sub>2</sub>O 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 Ti<sub>4</sub>Rh<sub>2</sub>O and Ti<sub>4</sub>Ir<sub>2</sub>O. 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 Ti<sub>4</sub>Ir<sub>2</sub>O 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-Ti<sub>2</sub>Ni 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 Zr<sub>4</sub>Rh<sub>2</sub>O<sub>x</sub>", Journal of Alloys and Compounds 796 (2019): 287-292.