

Insights into the crystal chemistry of uranium sulphides

Thanks to its 5*f* orbitals, uranium benefits from several valence states in inorganic compounds, from U²⁺ to U⁶⁺, and possesses a wide crystal chemistry. The radial expansion of these orbitals leads to energetically close crystal field (dominating in the case of 3*d* elements) and spin-orbit coupling (dominating in the case of 4*f* rare earths) interactions, and result in rich and exotic physical properties¹ (e.g. coexistence of superconductivity and ferromagnetism). When associated with a chalcogen element (Q = S, Se, Te), uranium forms inorganic compounds characterised by various crystallographic structures leading to unique uranium polyhedral environments,² with e.g. the presence of (S₂)²⁻ dimers.

In this context, binary and ternary uranium sulphides were synthesised at high temperatures in sealed evacuated silica tubes. Their crystal chemistry was then investigated in order to better understand the relationship between uranium oxidation state, chemical bonding and physical properties. High-resolution synchrotron X-ray spectroscopies reveal a predominance of U⁴⁺ together with mixed U³⁺/U⁴⁺ configurations in specific crystallographic environments, and highlight the more covalent character of the U-S bond compared to U-O. The investigation was extended to several families of ternary uranium sulphides U-*TM*-S, where *TM* is a 3*d* transition metal,³ illustrating how crystal chemistry can stabilise different uranium valence states depending on the local structural environment. The crystal chemistry of selected examples of compounds will be discussed in parallel to their physical properties.

References

- (1) Aoki, D.; Brison, J.-P.; Flouquet, J.; Ishida, K.; Knebel, G.; Tokunaga, Y.; Yanase, Y. Unconventional Superconductivity in UTe₂. *J. Phys.: Condens. Matter* **2022**, *34* (24), 243002. <https://doi.org/10.1088/1361-648X/ac5863>.
- (2) Mesbah, A.; Prakash, J.; Ibers, J. A. Overview of the Crystal Chemistry of the Actinide Chalcogenides: Incorporation of the Alkaline-Earth Elements. *Dalton Trans.* **2016**, *45* (41), 16067–16080. <https://doi.org/10.1039/C6DT02540D>.
- (3) Noël, H.; Troć, R. Magnetic Properties of Mixed Uranium and 3d Element Chalcogenides of the MU₈X₁₇ Type. *J. Solid State Chem.* **1979**, *27* (2), 123–135. [https://doi.org/10.1016/0022-4596\(79\)90151-8](https://doi.org/10.1016/0022-4596(79)90151-8).