Supporting Information: Complete Reference 27. Further details and input parameters for DFT calculations.

Structural Studies of TcO₂ by Neutron Powder Diffraction and First-Principles Calculations

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Reference 27. X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, D. C. Allan, *Comput. Mater. Sci.*, 25 (2002) 478.

We used a standard plane-wave code PWSCF 2.0.1¹¹ with optimized, norm-conserving pseudopotentials¹⁴ to represent the interaction between ions and electrons; semi-core states of Tc were included in its valence. An energy cutoff of 50 Ry was used on the plane-wave basis used in the representation of wave functions; the cutoff was 200 Ry for the representation of density. Crystal structure was determined through total energy minimization using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm and Hellmann-Feynman forces on atoms.

Integrations over Bloch vectors were sampled with a uniform 7 X 7 X 7 mesh (tested up to 9 X 9 X 9) in the Brillouin zone, and a Fermi-Dirac distribution with a broadening of 0.04 eV was used for smearing occupancies of electronic states. Ground state electron charge density and corresponding Kohn-Sham orbitals (which are energy eigenfunctions) emerging from the density functional theory calculations are

not directly useful in obtaining a precise picture of bonding. Here, we used a recently developed¹⁴ approach to construct localized Wannier functions. For crystals, they are obtained as a Fourier transform of extended Bloch functions that are smooth and periodic as a function of Bloch vector k . In the case of metals, normalization of a Wannier function (in this scheme¹⁴) corresponding to a given bond relates to its bond order. Wannier functions, as implemented in a plane-wave DFT code ABINIT²⁷ (with the same pseudopotentials and calculational parameters), were used in the present analysis.