Experimental report

07/08/2024

Proposal: 5-31-2949 **Council:** 10/2022

Title: Crystal and magnetic structure of Ruddlesden-Popper nitride Ce2TaN4

Research area: Materials

This proposal is a new proposal

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Samples: Ce2TaN4

Instrument	Requested days	Allocated days	From	To
D20	1	1	20/06/2023	21/06/2023

Abstract:

Ruddlesden-Popper (RP) type metal oxides are an important family of layered perovskite-derived materials with notable electronic and magnetic properties such as superconductivity in cuprates, e.g. doped-La2CuO4, and giant magnetoresistance in manganites. However, stoichiometric RP nitrides R1+nMnN1+3n (n = 1, 2, 3) had not until very recently been experimentally reported. We recently prepared the first K2NiF4-type nitrides and we have extended this work with discovery of the first mixed valent RP nitride CeIIICeIVTaVN4. Ce2TaN4 crystallizes in an orthorhombic variant of the n = 1 RP structure type. Powder neutron diffraction (PND) data are required for determination of accurate N positions, to check for the possibility of long range CeIII/CeIV charge order, as well as refinement of N-occupancies to check that no oxygen is present. The magnetic susceptibility of Ce2TaN4 has a ferro/ferri magnetic ordering observed at TC = 5 K. The ground state probably has a weak ferromagnetic (canted antiferromagnetic) spin order and PND data are also required to determine the magnetic structure below 5 K. 1 day on D20 is optimal for a small sample ~100 mg obtained from high-pressure synthesis

Experimental

Powder neutron diffraction was carried out on ~100 mg samples of Ce_2TaN_4 on the D20 High-intensity two-axis diffractometer in order to obtain a nuclear structure model as well as to obtain a model for a canted antiferromagnetic structure with T_N = 5 K. For the nuclear structure determination, temperature-dependent powder patterns were collected at 300K, 150K, and 1.6K in high-resolution mode with a neutron wavelength of 1.54 Å. High-flux measurements with a wavelength of 2.4 Å were carried out at temperatures of 15 and 1.6 K to calculate a difference diffraction pattern.

Results[1]

The nuclear structure of Ce_2TaN_4 was refined from high-quality powder patterns collected at several temperatures. Ce_2TaN_4 crystallizes in a orthorhombic distortion variant of the tetragonal Ruddelsden-Popper structure. Neutron diffraction was essential to reveal disorder on the nitrogen position manifesting in split positions. X-ray diffraction could not resolve this disorder owed to the large scattering contrast of Ce/Ta and N. We identified two sources of the disorder, the first is mixed valency of Ce+3/Ce+4, which is evidenced by short and long Ce–N interatomic distances. The second is a second-order Jahn-Teller effect of Ta^{+5}, resulting in a displacement of Tantalum from the centre of the TaN_6 octahedra. The tilt structure of the TaN_6 octahedra remains long-range ordered despite the disorder on the nitrogen positions.

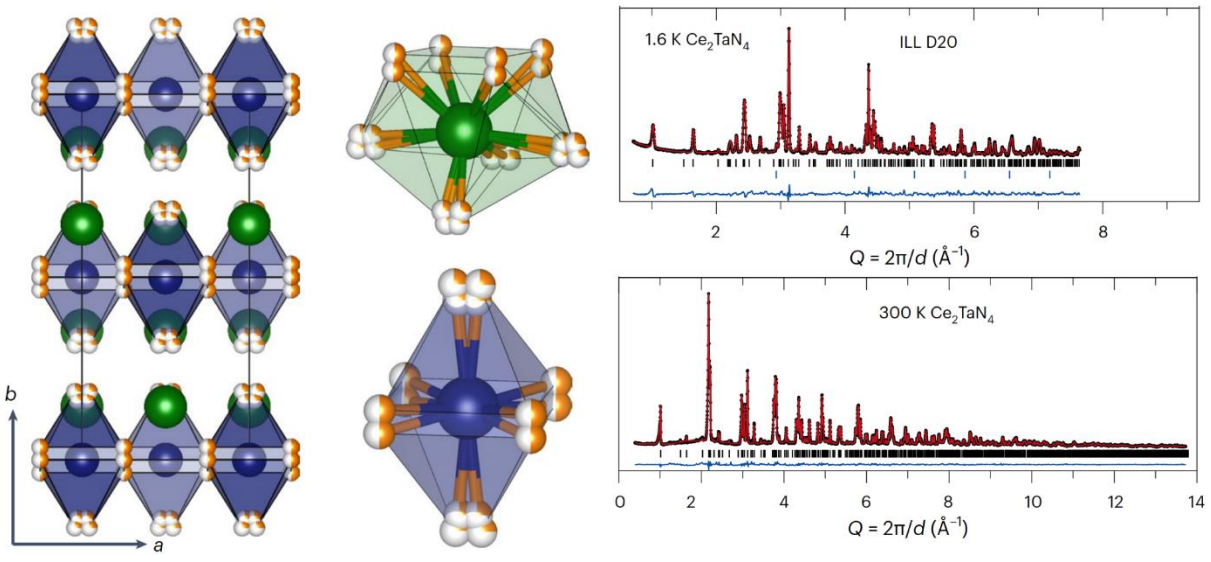

Fig. 1: Nuclear structure of Ce_2TaN_4 as well as Rietveld refinements of collected powder neutron data at 1.6 and 300 K.

The magnetic structure of Ce_2TaN_4 was solved from difference data and refined in Shubnikov group *Cm*'*ca*' and shows a magnetic moment of 1.4(1)μ_B per Ce^{3+} and a net ferromagnetic moment in the

order of the observed saturated magnetization. Ce^{3+}/Ce^{4+} was found to be disordered in agreement with the results of the nuclear structure refinement.

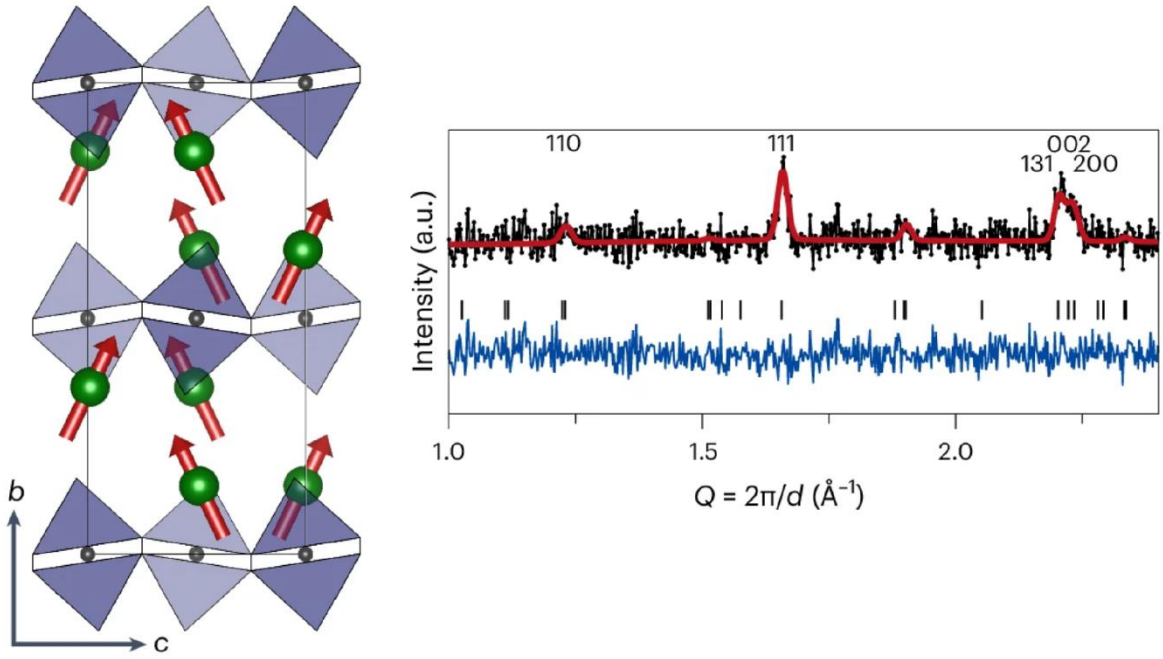

Fig. 2: Magnetic structure of Ce_2TaN_4 as well as refinement of the observed magnetic reflections.

Literature:

[1] Weidemann, M., Werhahn, D., Mayer, C. *et al.* High-pressure synthesis of Ruddlesden–Popper nitrides. *Nat. Chem.* (2024). https://doi.org/10.1038/s41557-024-01558-1