

MS21-P14 Nanoscale order in the frustrated mixed conductor $\text{La}_{5.6}\text{WO}_{12-8}$ Tobias Scherb¹, Simon A.J. Kimber², Christiane Stephan^{3,4}, Paul F. Henry⁵, Andrea Fantin¹, Gerhard Schumacher¹, Janka Seeger⁶, Justus Just¹, Adrian H. Hill⁷, John Banhart^{1,8}

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$\text{Ln}_n\text{WO}_{12}$ (Ln = Lanthanide) compounds are due to their mixed protonic/electronic conduction properties and their superior stability in acidic atmospheres highly potential materials for the use as gas separation membranes. We prepared pure samples of $\text{La}_{5.6}\text{WO}_{12-8}$, which showed exceptional device performance and stability, and studied the crystal structure in detail by the complementary use of neutrons and photons. The performance at temperatures above $T=600^\circ\text{C}$ is better than reported for other mixed conductors, and the comparable tiny water uptake (< 0.2 weight %), measured by TGA, suggests an unusually effective mechanism for proton transport. We report a comprehensive investigation of the average and local structure of $\text{La}_{5.6}\text{WO}_{12-8}$. Synchrotron x-ray and neutron powder diffraction show that a cubic fluorite supercell describes the average structure, with highly disordered lanthanum and oxide positions. On average the tungsten sites are six-fold coordinated, and we detect a trace (3.7(1.3)%) of anti-site disorder. In addition to sharp Bragg reflections, strong diffuse neutron scattering is observed, which hints at short-range order. We consider plausible local configurations, and show that the defect chemistry implies a simple 'chemical exchange' interaction that favors ordered WO_6 octahedra. Our local model is confirmed by synchrotron x-ray pair distribution function analysis and EXAFS experiments performed at the La K and W L3-edges. We show that ordered domains of around 3.5 nm are found, implying that mixed conduction in $\text{La}_{5.6}\text{WO}_{12-8}$ is associated with a defective glassy-like anion sublattice. The origins of this ground state are proposed to lie in the non-bipartite nature of the fcc lattice and the pairwise interactions which link the orientation of neighboring octahedral WO_6 sites. This 'function through frustration' could provide a means of designing new mixed conductors.

Keywords: neutron diffraction, PDF analysis, EXAFS**MS22** Beyond multipolar refinement

Chairs: Alessandro Genoni, Simon Grabowsky

MS22-P1 Identifying the correct metal atom in pairs of crystal structures of coordination compounds by aspherical-atom refinementClaudia M. Wandtke¹, Matthias Weil², Jim Simpson³, Birger Dittrich⁴

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Experimental multipole refinements on compounds containing metal atoms push the limit of classical charge density studies for various reasons. [1] The situation is different when conventional diffraction data of limited resolution are to be modelled by transfer of Hansen/Coppens multipole parameters [2] predicted by density functional theory, used as fixed scattering factors. Such procedures [3 and references therein] have so far mainly been used for organic compounds. Here we continue these developments and extend their applicability to coordination compounds.

It has been shown recently that the independent atom model can provide misleading results and does not allow to distinguish between neighbouring 3d metals, whereas aspherical modelling permitted their identification solely from single crystal X-ray diffraction data. [4] While the method is based on the Hansen/Coppens multipole model, the iterations involved are conceptually similar to Hirshfeld-atom refinement. [5]

In our current study several further 3d-metal complexes were studied. These were examples of pairs of published structures with nearly identical lattice constants but different metal atoms, where the differing chemical composition might already be questioned on chemical grounds, and where only diffraction data are available (e.g. in the form of a CIF and deposited structure factors). It is shown that aspherical-atom refinement then permits to identify and confirm the chemically most plausible metal atom in these metal-organic compounds.

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Keywords: invarium, coordination compound, validation**MS22-P2** Charge density and disorder in Al_2Ru Horst Borrmann¹, Michael Wedel^{1,2}, Lev Akselrud^{1,3}, Miroslav Kohout¹, Yu-Sheng Chen⁴, Tibor Koritsanszky⁵, Yuri Grin¹

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The simple intermetallic compound RuAl_2 exhibits remarkable physical properties, e.g. it is an unconventional semiconductor with narrow band gap [1]. In terms of structural features it is considered a parent structure and main building block for the family of Nowotny chimney Ladder (NCL) structures [2]. In contrast to the intriguing structures of most NCL compounds, the adopted TiSi_2 type structure is 'well behaved' as it is not modulated and therefore composite structure approach needs not to be applied [3]. In order to avoid problems due to inelastic scattering with Ag-target X-ray sources and in order to collect Bragg intensities up to very high resolution, diffraction data were collected at beamline ID-15-B of the Advanced Photon Source applying 30 keV X-rays. Since a large fraction of possible Bragg reflections is systematically weak, special efforts were necessary in order to extract reliable intensities from measured images. The fundamental approach as implemented in EVAL15 finally gave very good results [4]. The independent atom refinement already derives a model with excellent agreement, however, a faint indication of specific disorder is revealed. After applying the multipolar model according to Hansen and Coppens using XD-2006 [5], charge transfer from Al atoms towards Ru is clearly derived. Al_2Ru obviously is a more adequate description in perfect agreement with Si,Ti as given in the early determination of the parent structure [6]. Details of chemical bonding along with interpretation of detected disorder in terms of stacking faults will be discussed. Similar deviations in typically well-known structures seem to be quite common and deserve careful consideration.

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Keywords: intermetallic compounds, charge density, disorder