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### Chemical bonds in aluminium

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Recent advances in quantitative convergent beam electron diffraction (QCBED) [1], [2], [3] have led to the solution of an 82 year old problem – determination of the bonding electron density in aluminium. Until the present determination [4], [5], there was considerable disparity between a large number of experimental and theoretical determinations. These disagreements culminated in two recent theoretical studies where one asserted that bonding in aluminium is octahedrally coordinated [6] and the other that it is tetrahedrally coordinated [7].

In addition to the present QCBED determination, a density functional theory (DFT) first-principles calculation of the ground state electron distribution was performed. The QCBED and DFT determinations are in close agreement and show that the bonding electron density is concentrated exclusively in the tetrahedral interstices.

The detailed understanding of bonding in aluminium resulting from the present work has led to a new understanding of the influence of interatomic bonding on the mechanical anisotropy of aluminium. Correlations between bonding and the morphologies of precipitates that form in aluminium alloys have also been identified.

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### Polarized XAS of photosystem II and relevant Mn model complexes

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The Mn<sub>4</sub>Ca catalytic cluster of the oxygen-evolving complex (OEC) in Photosystem II (PS II) cycles through five oxidation states (S<sub>i</sub>-states, i=0-4) coupling the one electron photochemistry of the reaction center with the 4 electron redox chemistry of water oxidation. The structure of the Mn<sub>4</sub>Ca cluster has been extensively studied by X-ray [1] and other spectroscopic methods and by X-ray

crystallography between 3.8-2.9 Å resolution [2-5]. The most recent X-ray crystallography structure is at 1.9 Å resolution [6]. Radiation damage to the Mn<sub>4</sub>Ca cluster, although much reduced in the most recent structure at the highest resolution, still remains a limiting factor [7].

We have previously reported detailed X-ray absorption spectroscopy studies from solution and single crystal XANES and EXAFS data from the native S<sub>1</sub> (dark) state and proposed structural models of the Mn<sub>4</sub>Ca cluster of PS II within the context of the protein environment [1, 8]. This study used PS II dimer crystals obtained from *T. elongatus*, in which the crystal unit cell contains four PS II dimers. The structural parameters derived from X-ray spectroscopy in relation to the X-ray crystallography structure at 1.9 Å will be discussed. We have also collected polarized spectra of monomer PS II single crystals, which have been recently crystallized [9]. Monomer crystals have a favorable orientation for deriving a unique structure for the Mn<sub>4</sub>Ca cluster.

We have extended the study to the higher S-states by illuminating the S<sub>1</sub> state solution and single crystals either by continuous illumination or by laser flashes to create intermediate S-states (S<sub>2</sub> and S<sub>3</sub>). The solution state spectra show changes in the structure of the catalytic cluster as it advances through the intermediate states. Polarized XANES and EXAFS spectra from these crystals show unique orientation dependence and provide additional information about the structural changes taking place in these intermediate states. The relevance of the geometric and electronic structural changes derived from the XAS studies to the mechanism of water oxidation will be discussed.

The polarized XAS data from crystals of many multinuclear oxo-bridged Mn complexes have been collected. The polarized spectra have been used to understand the electronic structure of the Mn complexes, and these studies provide information that will be useful for understanding the structure and the mechanism of the Mn<sub>4</sub>Ca cluster present in PS II.

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### The synergism of XAS and crystallography

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In recent years, research on metalloproteins has benefited from synergism between bioinformatics, sample characterization, spectroscopy, and structural methods. The combination of these methods results in a pipeline that helps to establish an excellent basis for understanding necessities and variability of metal binding.

Bioinformatics is the established method to identify conserved