

Dear Dr Evans

I would like my thesis entitled "The Structure and Negative Thermal Expansion of Low-Dimensional Compounds" to be considered for the PANalytical Thesis Prize for Physical Crystallography. The thesis was submitted in September 2010 and the degree approved following the viva in February 2011.

The thesis details the preparation and properties of previously unknown mixed-metal copper, silver and gold cyanides, $(M_xM'_{x-1})CN$, which contain infinite metal-cyanide chains. These compounds are fascinating because they all exhibit one-dimensional negative thermal expansion (NTE). The magnitude of the NTE effect is dependant on the packing of the chains, in turn determined by the composition. The results from the NTE studies were published in *Z. Kristallogr.*, 2010, **225**, 457-462. The phase diagrams for each bimetallic system, $(M_xM'_{x-1})CN$, have been explored and the structures of these poorly-crystalline, disordered materials determined using total neutron diffraction data collected on GEM at the ISIS neutron source. There is a paper in preparation, which describes the detailed structures of these disordered cyanides, together with the photophysical measurements of these potentially important luminescent materials.

The final chapter of the thesis, summarised in *Inorg. Chem.*, 2011, **50**, 104-113, reveals the true and previously unknown nature of palladium and platinum cyanides. These compounds have been known to science for over two centuries but it was only last year that their structure was established. Palladium and platinum cyanide both sit at a unique juncture between disordered and nanocrystalline materials and hence their structure solution was complicated. The particles in these materials consist of small disordered stacks of metal-cyanide sheets containing vertex sharing square-planar $M(CN)_4$ units, where the size of each sheet is typically around 3×3 nm. The small size of the crystallites means that the sheets' edges form a significant fraction of each material. In each case, half of the terminal cyanide groups are replaced by small neutral molecules to achieve charge neutrality within the sheets. Total neutron diffraction studies identified that the $Pd(CN)_2$ nanocrystallites are terminated by water molecules and the $Pt(CN)_2$ nanocrystallites by ammonia. To succeed in identifying the species around the edges of nano materials is unusual.

Yours Sincerely

Edward Bilb 