Exploiting the Tunable Wavelength Capabilities of Beamline I19

Karim J. Sutton[a,b], Kirsten E. Christensen[a], Amber L. Thompson[a], Richard I. Cooper[a]
Harriott Nowell[b], Sarah A. Barnett[b], David R. Allan[b]

[a]Chemical Crystallography, Chemistry Research Laboratory, Oxford, OX1 3TA
[b]Diamond Light Source, Chilton, Didcot, Oxon OX11 0DE

Introduction

Anomalous scattering experiments using synchrotron X-ray radiation allow the discrimination of multiple oxidation states within a single crystal structure. Additionally, macromolecular methods, such as MAD phasing can be applied to low resolution small molecule data.

Beamline I19 at Diamond Light Source has been designed to enable anomalous dispersion studies on single crystals using a tunable wavelength, fixed exit monochromator.[1] These experiments make it possible to differentiate between oxidation states of atoms; discriminate between atoms with near-identical X-ray scattering factors; and solve the phase problem for very low resolution X-ray data.

Anomalous Scattering

➤ Anomalous scattering is observed due to resonance between the energy of the incident X-rays and the electronic transition energy of core electrons.
➤ This results in an increment to the normal scattering factor:[2]

$$f = f^0 + |f^\Delta|e^{i\delta} = f^0 + f' + f'' \quad [1]$$

➤ The imaginary part of the anomalous scattering determined using the Optical Theorem:[3]

$$f''(E) = \frac{mc\varepsilon_0 E\mu_a}{e^2\hbar} \quad [2]$$

➤ The real part of the anomalous scattering can thus be obtained using the Kramers-Kronig[4] relation:

$$f''(E_0) = \frac{2}{\pi}\oint \frac{Ef''(E)}{E_0{}^2 - E^2}dE \quad [3]$$

Determination of Anomalous Scattering Factors

Commissioning of a fluorescence detector on I19 allows for the direct measurement of X-ray absorption with respect to the energy and hence f'' and f' through equations [1] and [2] respectively. In the vicinity of the absorption edge f' (blue) and f'' (red) change rapidly and extra features are observed due to EXAFS and XANES.

* *
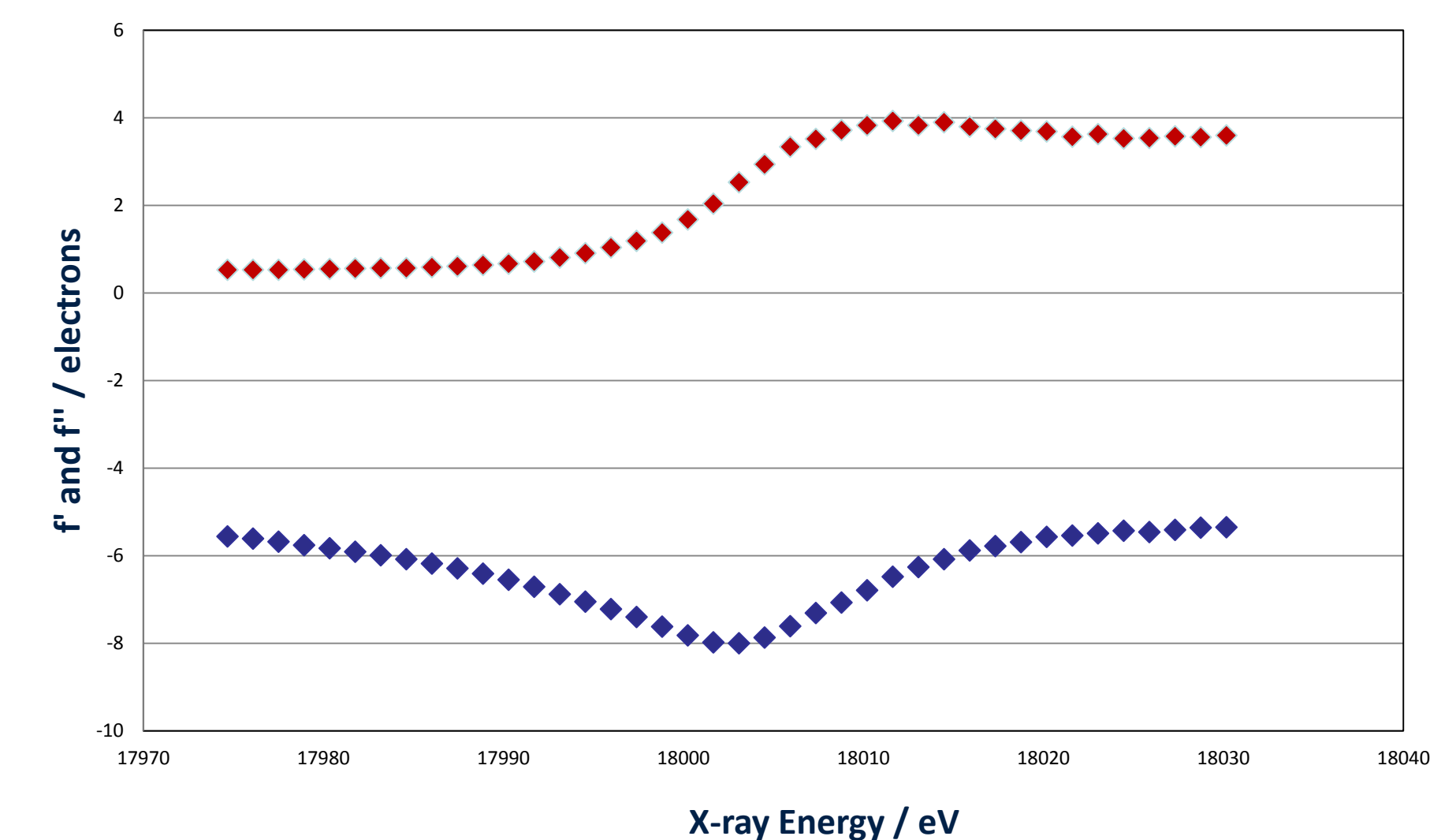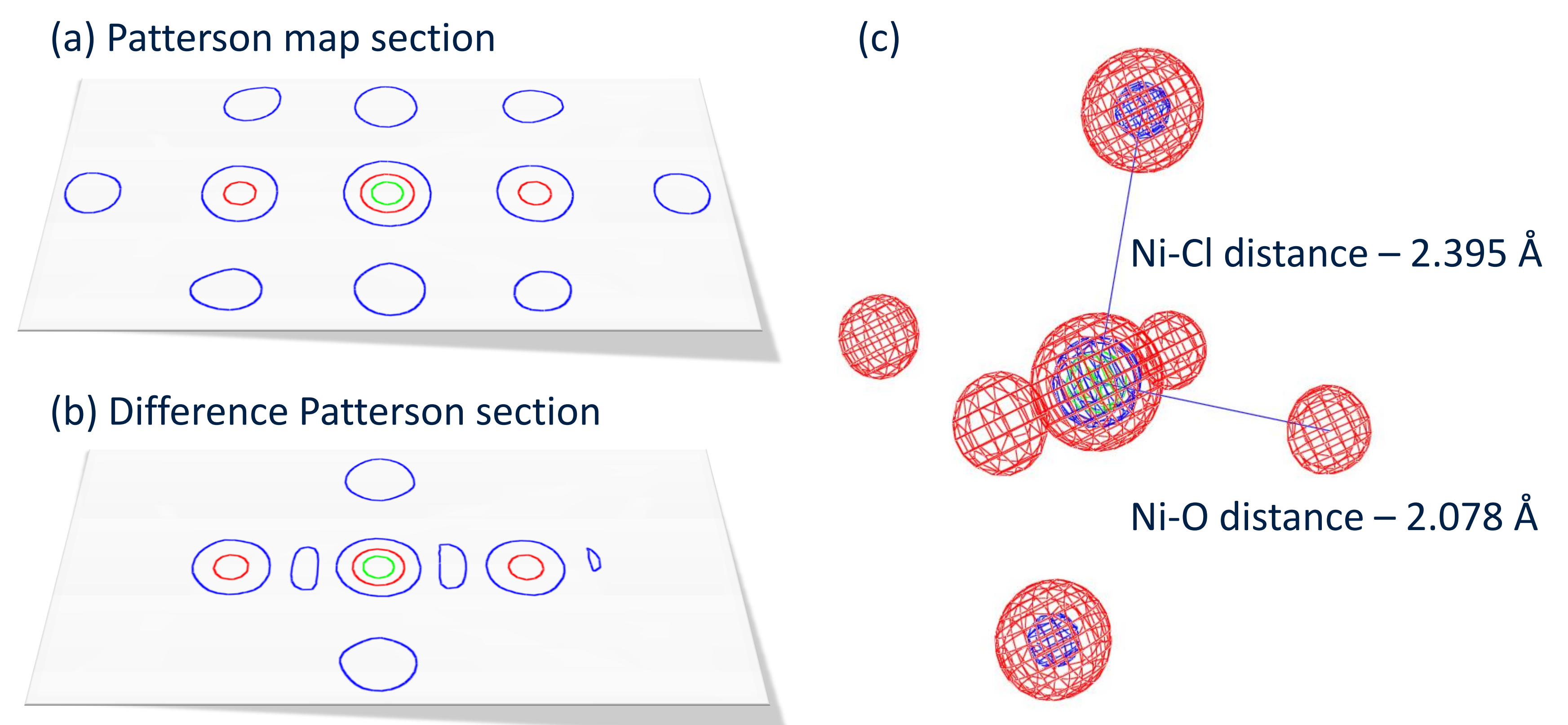
Oxidation State Discrimination
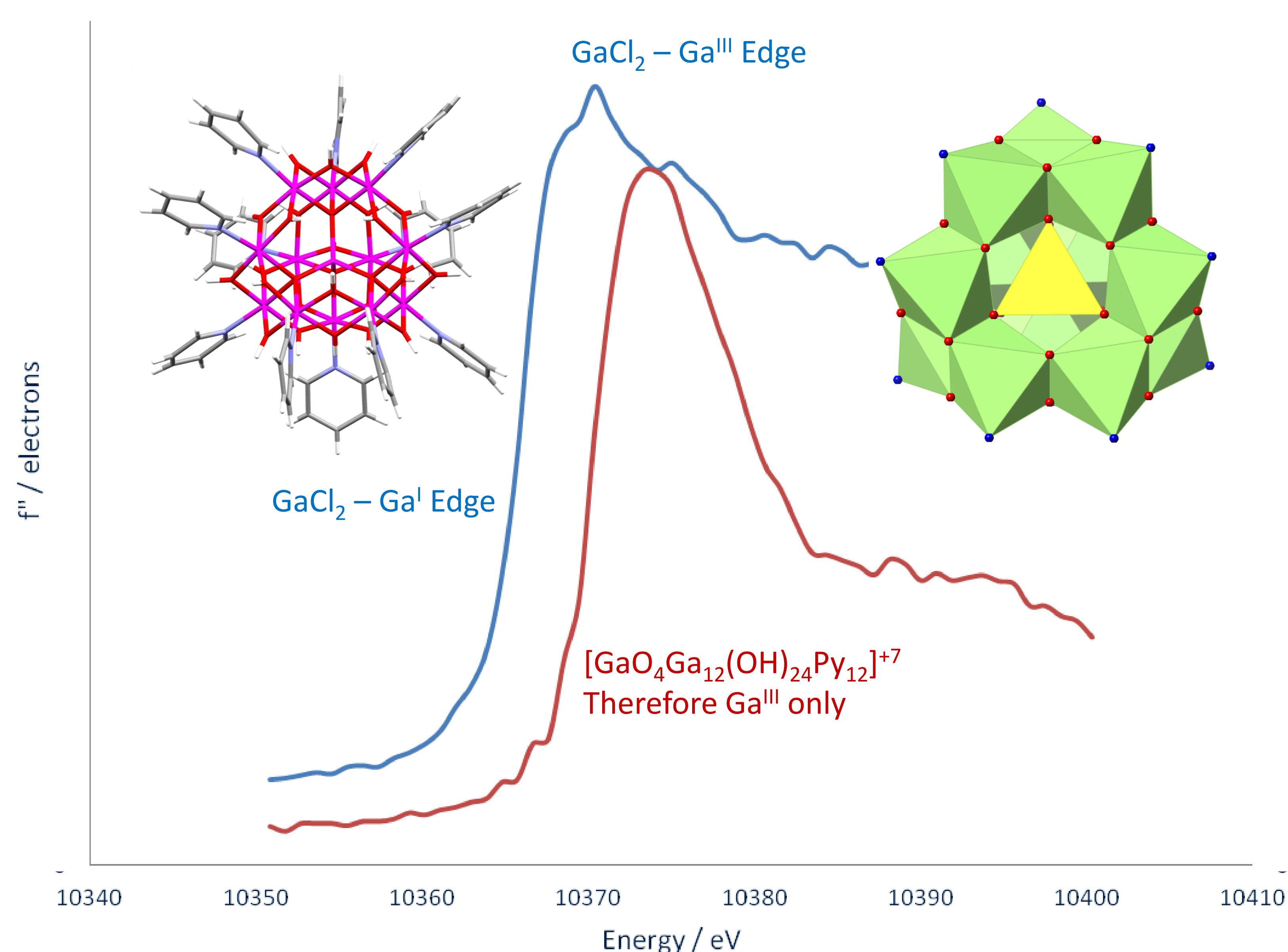
Anomalous scattering occurs as a result of resonance between the energy of incident X-ray radiation and energies of electronic transitions within an atom. Since these transition energies vary as a function of the number of electrons in the core, the position of the absorption edge consequently changes with oxidation state. Therefore a fluorescence scan across the absorption edge of a mixed-valence compound (e.g. $GaCl_2$) is a product of two similar profiles (for Ga(I) and Ga(III)) with an offset of ~5 eV.[5]

The fluorescence scan for $GaCl_2$ (blue) reveals a second peak about 5 eV from the first edge (in keeping with results presented by Wilkinson and Cheetham).[5] Fluorescence of a Ga_{13} cluster (red), containing only the Ga^{3+} ions, reveals just one edge at a higher energy than the onset of the Ga^+ edge in gallium dichloride. By subsequently recording datasets on such mixed-valence materials at multiple wavelengths so as to maximise differences in f' and f'' (between the datasets), we are able to resolve both the charge *and* positions of the ions.

Structure Solution

(a) Patterson map section

(b) Difference Patterson section

(c)

Ni-Cl distance – 2.395 Å

Ni-O distance – 2.078 Å

Multiple Anomalous Diffraction (MAD) phasing is regularly employed in macromolecular structure solution, taking datasets at multiple wavelengths in order to maximise $\Delta f'$ and $\Delta f''$, and therefore the anomalous signal. Additionally, difference Patterson Maps (Buerger, 1942) can be used to solve the rest of the structure.[7] The SuperNova dual source diffractometer in Oxford allows for data collection at two wavelengths (Mo – 0.7107 Å and Cu – 1.5418 Å). The position of the Ni absorption edge (1.4879 Å) in relation to these is such that there is a significant enough discrepancy in the anomalous scattering factors to produce a difference Patterson map for a $NiCl_2.6H_2O$ sample. A difference Patterson map shows only vectors between the anomalous scatterer and other atoms in the structure. The figure above shows generalised Patterson sections in the Cl-Ni-O plane using (a) coefficients of $F_o{}^2$ and (b) $Fo_{Cu}{}^2 - Fo_{Mo}{}^2$. The three dimensional difference Patterson is shown in (c).

Conclusions

➤ Mixed valencies within a single crystal can be detected using fluorescence scans.
➤ Both the charge and position of ions can be resolved by refinement of different species by applying the appropriate f' and f'' values.
➤ Macromolecular anomalous dispersion based structure solution methods (MAD phasing) can be applied to low resolution small molecule data.

References

[1] H. Nowell, Sarah A. Barnett, Kirsten E. Christensen, Simon J. Teat and David R. Allan, *J. Sync. Rad.* **2012**, 19.
[2] G. Evans and R. F. Pettifer, *J. Appl. Cryst.* **2001**, 34, 82-86.
[3] R. W. James, *The Optical Principles of the Diffraction of X-Rays*, **1969.**
[4] J. J. Hoyt, D. Defontaine and W. K. Warburton, *J. Appl. Cryst.* **1984**, 17, 344-351.
[5] A. P. Wilkinson and A. K. Cheetham, *J. Appl. Cryst.* **1992**, *25*, 654-657.
[6] W. A. Hendrickson, J. L. Smith and S. Sheriff, *Meth. Enzymol.* **1985**, *115*, 41-55.
[7] M. J. Buerger, *Proc. Natl. Acad. Sci. U. S. A.* **1942**, *28*, 281-285.