

The Influence of Li Intercalation on the  
Electronic Polarisability of Oxide Lattices  
Determined by XPS.

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Abstract.

X-ray photoelectron spectroscopy (XPS) is known, mainly, as a technique for surface analysis. It is especially valued for the information that it provides on chemical state by means of the chemical shift. This chemical shift depends on the magnitude of two distinct contributions; firstly that from the initial state of the ion, the Madelung potential etc, and, secondly, that from the final state of the ion. This final state contribution stems from the relaxation, or polarization, of the surrounding ligands following the core photo-ionization event. Intercalation of ions such as lithium can be expected to influence this second contribution by its influence on the electronic polarizability of the oxygen ions and by its influence on the lattice parameters. The effect of this on the binding energy is rather small but is magnified in its influence on a related process – the emission of an Auger electron following core ionization. A measurement that is sensitive to this effect is known as the Auger parameter (AP). The AP is the difference in kinetic energy of the Auger peak in the spectrum and that of the principal photoelectron peak, calculated by an internationally accepted procedure. It has been shown in recent publications (Moretti, Satta, and Phillipone Surface and Interface Analysis, to be published, April 2001) that it is possible to calculate an AP for the free ion from the known crystal structures of relevant oxides. The free ion value is the baseline value for an ion that is not subjected to any final state effects. From this baseline the influence of oxygen ion polarizability on the AP becomes interpretable and measurements of AP as a function of intercalation or of the formation of mixed oxides then reveal directly the effect of this on polarizability. Polarizability is crucial to the dielectric properties of oxides, such as refractive index and is of value in optimizing intercalation compounds for use in opto-electronic devices.

The use of this methodology will be illustrated by measurements made for the system  $\text{Ce}_2\text{O}_3/\text{V}_2\text{O}_5$ . (Salvi, Decker and Guascito, Surface and Interface Analysis, to be published, April 2001) For this purpose a new in situ cell for electrochemical intercalation from organic electrolytes has been developed as an attachment to the XP spectrometer. The advantages of in situ (anaerobic) intercalation will be outlined and initial results compared with those made *ex situ*.