Connecting experimental valence EELS to the electronic structure using density functional theory: methods and applications.

Keast, V.[1]

[1] The University of Newcastle, Australia

Recent years have seen an increase in the interest and application of the low-loss region (<~50 eV) in electron energy-loss spectroscopy (EELS). The spectral detail in this region is associated with excitations of the valence electrons and includes interband transitions and collective excitations. As a consequence, this valence EELS displays a rich and complex array of spectral features. In principle the valence EELS can provide important information about the electronic structure, optical properties and bonding of materials. Although delocalisation effects prevent the acquisition of information at the sub-nanometre scale, the resolution possible with EELS still far exceeds that can be obtained with optical techniques.

Despite these advantages, the analysis of the fine structure with the valence EELS has not been extensively applied, with the exception of studies of localised surface plasmon resonances. The difficulty lies in the interpretation of the complex array of spectral details. Calculations of the valence EELS can be performed by first calculating the ground state electronic structure using density functional theory (DFT), which is then used to determine the response functions. In the independent particle approximation the electron and hole generated are assumed to not influence the other electron states and to not interact with one another. That is, quasiparticle and excitonic effects are ignored. This approach has been successfully applied to predict the overall spectral shape of a number of materials, especially metals. However for many materials, particularly semiconductors and insulators but also some metals, the spectral details are not well reproduced. Bandgaps, when present, are always underestimated and in the worst cases the calculations completely fail to predict the spectral shape.

The valence EELS is directly connected to optical response functions (e. g. the complex dielectric function) and there are a number of sophisticated computer codes already available to calculate these, where quasiparticle corrections can be introduced with the GW approximation and excitonic effects with the Bethe-Salpeter equation (BSE). In some cases the inclusion of local field effects (LFE) and exploration of the momentum dependence is also important. In some cases these computationally expensive approaches can be avoided by instead by using alternative exchange-correlation potentials. Examples demonstrating the effects of these higher order corrections will be presented and a discussion of when and why they are necessary will be given. A range of silver, copper, cadmium and zinc oxides and sulphides will be discussed as well as ionic materials such as KBr.