

EELS NEAR EDGE STRUCTURES

A tool for probing the structure properties, the unoccupied electronic states and the oxidation state of metal oxides.

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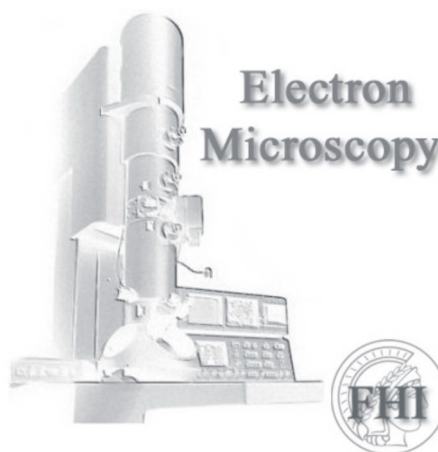
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The Energy Loss Spectrum

The principle of electron energy loss spectroscopy (EELS) is quite simple: A fast electron interacts with matter, and the energy loss of the electron is measured. The probability of an interaction over energy loss is called a loss spectrum. Features in the spectrum can be attributed to various inelastic interactions such as plasmon excitation and ionisation processes which are characteristic for each element. Transitions in an ionisation process can only take place to electron states which are empty: like x-ray absorption spectroscopy, EELS gives information on the density of unoccupied states above the Fermi level. Most common used spectrometer are attached to the bottom of the camera chamber of the TEM (post-column spectrometers) and use the fact that electrons of different energy follow different paths in electric and magnetic fields.

The Densities of States Interpretation

Transitions of the excited electron from initial to final state are described by

$$I \propto |M_{i,f}| \cdot N(E).$$

$|M_{i,f}|$ is the matrix element which represents the overlap integral between the initial state and the final state and $N(E)$ is the more commonly known density of states (DOS). In order for a transition to be observed, there must be an overlap between the core states and the final wavefunctions. The matrix elements also imply the dipole selection rule which allows transitions from an initial state of angular momentum l only to final states of angular momentum $l \pm 1$. The matrix elements therefore allow to probe the local DOS of each chemical element separately according to different angular momentum quantum numbers. Because the core-level states are highly localized, $N(E)$ is a local density of states (LDOS) at the site of the excited atom. As a result, the observed DOS is a symmetry-projected density of states. Thus, as an example, modulations in K-edge intensity (1s initial state) reflect mainly the density of 2p final states.

Many properties of solids can be expressed in terms of the DOS: for example, in a metal, all the transport, magnetic, and thermal properties of the electrons depend upon the density of states at the Fermi level.

In order to gain information about the bonding mechanisms, features in the spectra must be well understood so as to appreciate how the changes in near edge structure relate to changes in electronic structure. Ab-initio band structure calculations therefore provide a powerful tool for the interpretation of the energy loss near edge structure (ELNES) [1-3].

Applications of Energy-Loss Spectroscopy

Elemental Analysis

Elemental analysis is the most frequent electron-microscope application of EELS. Most commonly it is used for analysing elements of low atomic number, which are difficult to quantify by EDX spectroscopy. Analogue to XAS, EELS provides information about electronic states around the selected atoms, although XAS typically shows a much better energy resolution than EELS. However, the advantage of EELS is its very high spatial resolution down to the nanometer level.

Structural Information

Inelastic scattering in a solid is sensitive to the crystallographic and electronic structure of a specimen as well as to its elemental composition. This structural information is present in the dependence of the inelastic intensity on specimen orientation, in the angular dependence of scattering, and in the form of fine structure in the low-loss or core-loss regions of the energy-loss spectrum. The choice of a scattering vector allows selection of particular final crystal orbitals for the transitions in question [4-7]. Anisotropy in the density of unoccupied states can therefore be detected in the fine structure of ionisation edges in angle resolved EELS. Based on the comparison of experiment and theory, it is possible to associate details of the spectra to density of states and band structure features.

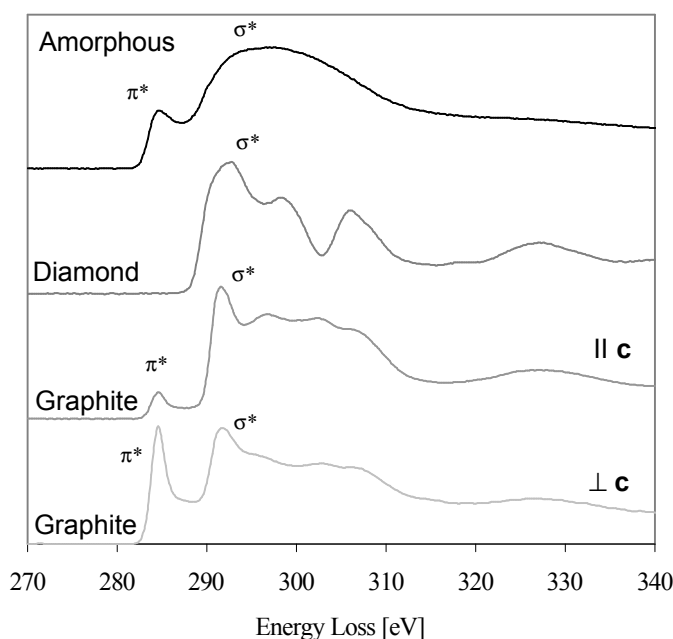


Fig. 1: The effect of structural variation on the shape of the ionisation edge is exemplified for the carbon K-edge in amorphous carbon, Diamond and Graphite. Due to the anisotropy of Graphite, the ELNES depends on the orientation of the crystal relative to the direction of the incident electron beam (electrons entering the sample parallel or perpendicular to the crystal c-axis). (Courtesy of H. Sauer).

Determination of Valency from White-Line Ratios

The L_{23} edges of transition metals and M_{45} edges of rare earths are characterised by two white-line peaks close to the ionisation threshold. The energy separation of these peaks reflects the spin-orbit splitting of the initial states in the transition. Although their relative intensity need not correspond to the number of electrons in the initial states, numerous EELS experiments have shown that a change in valence state of cations introduces a dramatic change in the intensity ratio of the white lines [8,9]. White-line measurements are therefore a potential source of information about oxidation state.

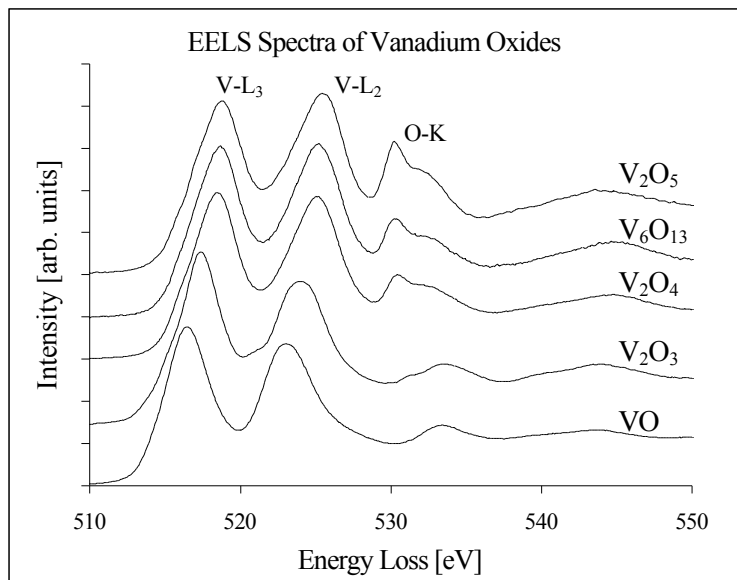


Fig.2: Vanadium L-edge and oxygen K-edge of different vanadium oxides. Changes in the oxidation state of vanadium are reflected by the variation of the O-K edge shape and a varying intensity ratio of the two V-L edges.

Chemical Shift

The chemical surrounding of an atom in a compound determines the charge distribution of its valence band. The resulting effective potential on that atom is related in varying degrees to all the electronic levels of that atom and therefore gives rise to an energy shift in a spectrum [10]. In case of vanadium oxides, for example, the chemical shifts of the V 2p peaks are characteristic for the different vanadium valences in the series presented in fig 3.

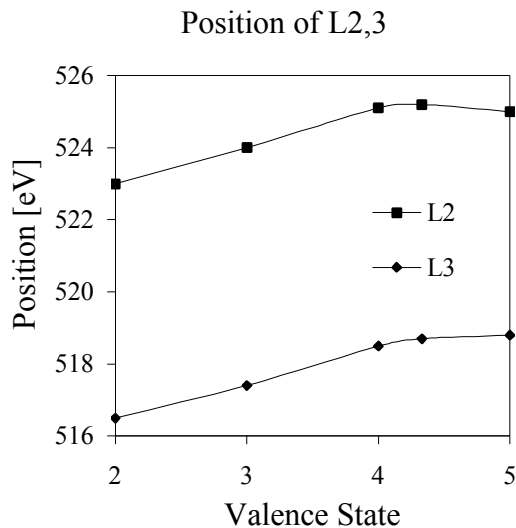


Fig.3: The chemical shift of the Vanadium L edge to higher energies with increasing oxidation state results from a reduced screening of the positively charged nucleus with decreasing 3d occupancy.

References

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Further reading

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