Electron Energy Loss Spectroscopy

Chemical Information at the Nanometer Scale

The combination of high resolution imaging with energy loss spectroscopy allows to resolve questions about the morphology, structure, composition and electronic structure of a material in a single instrument. By the assistance of band structure calculations and simulated EELS spectra, the experimental data can be analyzed in detail. Following this approach it is possible to study the relation between the geometric and electronic structure of materials at the nanometer scale.

Introduction

Progress in materials science and nano-technology is closely connected with the availability of instruments that allow to study the morphology, geometric structure and chemical composition of materials at the nanometer scale. Modern analytical transmission electron microscopes (TEM) for sure fulfill this task in an unsurpassed way. Observation over a large range of magnifications, dark and bright field imaging, electron diffraction, tomo-graphy and holography are some of the imaging techniques that can be used in a well equipped analytical TEM. In addition to the imaging capabilities, there is the spectroscopic part and most analytical instruments are equipped with energy dispersive detectors for the detection of characteristic X-rays or electron energy losses caused in inelastic interactions between the probing electrons and the sample material. Especially electron energy loss spectrometry (EELS) is used for the characterization of inelastic scattering processes over a wide energy range. In fact, a TEM offers optimal conditions for performing inelastic scattering experiments: the beam of electrons can be focussed down to very small probe sizes and the scattering properties can be investigated at very high spatial resolution while at the same time, information about the geometric structure of the sample is provided by the imaging capabilities of a TEM. In addition, the electron gun provides a source of close to mono energetic electrons. One therefore simply needs to analyze the amount of energy the probing electron has lost during its passage through the sample. The energy loss spectrum is then generated by recording the number of electrons that have lost a certain
As such, the recorded spectrum resembles the probability of an inelastic interaction as a function of the transferred energy. Compared to EDX, the main advantages of EELS are the much better energy resolution and a higher sensitivity for light elements. In general, an EELS spectrum can be divided into zero loss, low loss and core loss region. The zero loss is the most intense feature and represents electrons that passed the sample without losing energy plus those which have excited phonon modes for which the energy loss is less than the experimental resolution. Plasmon and valence band excitations appear at low energy losses up to about 50 eV while core shell excitations appear at atom characteristic ionization energies at higher energy loss. The whole range therefore contains valuable information not only about the elemental composition, but also about the electronic, optical and mechanical properties of a material.

The Energy Loss Near Edge Structure

In a simplified picture, the process in which an electron of the beam excites a core electron of an atom through a transfer of a momentum q in a Coulomb like interaction can be imaged as shown in figure 1.

The transition of the excited electron from the initial core state to an unoccupied state above the Fermi-level is determined by the direction of the momentum q and the transferred energy. In fact, the direction of the transferred momentum determines if a transition from e.g. an initial s state takes place to a final state of predominant px, py or pz character. The transition is accompanied by the dipole selection rule, which in general applies for energy losses that are small compared to the initial energy of the probing electron (which is usually 200 to 300 keV in a TEM). In addition, the final state is restricted by the requirement of a non vanishing overlap between the initial and final state wave function. While the energy onset of
an ionization edge is determined by the atom kind, the initial core state, and eventually, the oxidation state of the atom, the actual cross section for a transition is, to a first approximation, proportional to the number of available final states. The fine structure observed above the edge onset in an EELS spectrum therefore monitors the angular momentum projected density of states at the corresponding atomic site (see the right part of figure 1 where the density of unoccupied states is plotted and a simulated edge is indicated by the red curve). As such, the energy loss near edge structure (ELNES) is very sensitive to the electronic structure of a material. It is worthwhile to note here that the ELNES is very similar to the near edge structure observed in X-ray absorption spectra (XANES), where instead of an electron, a photon transfers energy and a final state is selected according to the directionality of the photons polarization. Figure 2 shows the remarkable similarity between ELNES and XANES for the case of a spectrum recorded from a vanadium phosphorous oxide. The main difference between the two results from the higher energy resolution obtained in the X-ray absorption spectrum. Three main features can be observed in the spectrum. The first two, peaking at around 518.7 and 525.3 eV, correspond to the vanadium LIII and LII edges, respectively. These peaks, resulting from sudden increase of the inelastic scattering cross section, appear because here the transferred energy fits exactly the energy required to excite a vanadium $2p_{3/2}$ or $2p_{1/2}$ electron, respectively. According to the dipole selection rule, states of predominant 3d character above the Fermi level are selected as final states. The shape and structures of the two peaks is complicated by multiplet effects and therefore does not directly resemble the density of unoccupied 3d states in the vicinity of the excited atom. The situation is slightly less complicated for the oxygen K edge which starts at about 530 eV. Here, the transition takes place from an oxygen 1s to a final state with 2p character at the oxygen atom. In this case, there are no multiplet effects and the shape of the oxygen K edge closely mirrors the portion of 2p character in the density of unoccupied states. Of course, spectral broadening due to the limited resolution of the spectrometer, the energy spread of the initial beam and lifetime effects have to be taken into account. The availability of simulated spectra is crucial for an in-depth interpretation of recorded spectral features. Without them, the instruments analytical power is certainly wasted. Basically, there exist two approaches for the calculation of EELS spectra: real space multiple scattering and density functional theory based band structure codes [1, 2]. The close agreement between simulation and experiment is demonstrated in figure 2 for the case of the oxygen K edge (orange curve). Using these calculations, it is possible to determine the contribution of differently coordinated atoms of the same kind to the total spectrum as shown in figure 3.
linear combination of atomic orbitals (LCAO) picture [3]. The simulation reveals that the first feature in the oxygen K edge, appearing between around 527 and 535 eV, arises from transitions to final states that are dominated by unoccupied vanadium 3d states with some admixture of oxygen 2p character. The shape of the oxygen K edge in this region therefore resembles the electronic structure at the distorted VO$_6$ structural units present in β-VOPO$_4$. Even crystal field effects can be seen: the main peak and its shoulder correspond to transitions into either π* or σ* final states formed between the oxygen 2p and vanadium 3d states. Intensity in the higher energy range of the oxygen K edge starting from about 535 eV arises from transitions to final states that are dominated by oxygen 2p-phosphorous 3sp combinations [3]. How sensible the ELENS is to the arrangement of atoms and its application in the characterization of nanoscopic materials is demonstrated in the following. Figure 4 shows medium and high resolution TEM images of V$_2$O$_5$ nanorods [4]. From the literature it is known that, besides the ordinary V$_2$O$_5$, there exists a polymorph with a slightly altered arrangement of structural units named γ-V$_2$O$_5$. The EELS spectra recorded from the nanorods and a reference spectrum of V$_2$O$_5$ are shown in figure 4. A comparison reveals that the shape of the vanadium LIII and LII edges are similar in the two spectra. Their energy position and intensity ratio depend very sensitively on the oxidation state. From the agreement it can be concluded that the nanorods contain vanadium in a V$+^+$ oxidation state. An obvious difference between the two spectra is observed in the region of the oxygen K edge. By the use of simulated spectra, the shape of the oxygen K edges can be understood and unambiguously assigned to the underlying geometric arrangement of the atoms. EELS recorded from the nanorods therefore reveal that they are crystallized in the structure of γ-V$_2$O$_5$ [4].

**Summary**

A TEM provides ideal conditions for performing inelastic scattering experiments. The spectra can be recorded at high special resolution and provide information about the electronic structure of a material over a large energy range, including plasmon and valence band excitations as well as core shell excitations. Due to the high energy resolution, EELS is very sensitive to even slight changes in the electronic structure and in many cases theoretical calculations are needed in order to understand the recorded features. In this short article, not all aspects of EELS could be covered. The discussion of beam sensitivity and irradiation induced artefacts in the spectrum has been left out, although especially the above presented vanadium compounds are very beam sensitive and special care has to be taken during spectrum acquisition. Also some important techniques such as energy
filtered imaging and spectrum imaging have not been discussed here.

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