MAX-PLANCK-GESELLSCHAFT

Micron, 34 (2003) 3-5, 235-238

High resolution EELS using monochromator and high performance spectrometer: comparison of V_2O_5 ELNES with NEXAFS and band structure calculations

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Submitted 20 October 2002; accepted 10 February 2003

Abstract (9)

Using single crystal V_2O_5 as a sample, we tested the performance of the new aberration corrected GATAN spectrometer on a monochromatised 200 kV FEG FEI (S)TEM. The obtained V *L* and O *K* ELNES were compared with that obtained in a common GATAN GIF and that in the new spectrometer, without monochromatised beam. The performance of the new instrumentation is impressive: recorded with an energy-resolution of 0.22 eV, the V L_3 edge reveals all the features due to the bulk electronic structure, that are also revealed in NEXAFS with a much higher energy-resolution (0.08 eV). All features of the ELNES and NEXAFS are in line with a theoretical spectrum derived from band-structure calculations.

Keywords: Monochromator, ELNES, NEXAFS, energy-resolution, DOS, V_2O_5

Introduction

The combination of electron energy-loss spectrometer (EELS) with a transmission electron microscope (TEM) exhibits the advantage of high lateral resolution for chemical analysis and for structural determination by means of electron diffraction and high-resolution imaging. The near edge fine structure (ELNES) of a core-level energy loss spectrum is related to the momentum resolved density of unoccupied state at the site of the excited atom [1]. The application of ELNES-analysis extends to all fields of materials science to explore the local chemical and electronic structure at a nanometer scale [2]. However, commercially available EELS/TEM system usually prevents an energy-resolution much better than 1 eV even with field emission gun. As a consequence much of the fine structure in ELNES that carries invaluable information about geometric and electronic structure is washed out. For high-resolution data the comparison to state-of-the art theory would be possible, improving drastically the reliability of spectral interpretation.

Recently, FEI has constructed a monochromatised 200 kV (S)TEM which aims at the 0.1 eV energy resolution level for EELS. This microscope has now been installed at the Centre for HREM at Delft University. The improved energy resolution is due to several factors: (a) the energy spread of a Schottky field emitter is reduced by a Wien filter monochromator positioned directly after the field emission gun. (b) the 200 kV high tension tank was improved by adding mechanical as well as electrical damping elements [3]. At the same time, GATAN has developed a high resolution

energy filter that has more stable electronic as well as improved electron optics [4]. The electron optics of the new spectrometer comprises additional multipol lenses in front of the magnetic prism, which eliminate 3rd and some of the 4th order spectral aberrations. Therefore, the TECNAI with Wien filter monochromator, optimised high tension tank and improved GATAN image filter, opens a new era for the high energy resolution ELNES and their applications in solid state physics/chemistry and in materials science.

Although high-energy resolution EELS may become commercially available in the near future, two fundamental questions still need to be answered: (i) how is the performance of the system compared to known techniques as NEXAFS (ii) to which extent can we explore the electronic information of investigated solid state materials. In our previous work, the electron optical performance of the new spectrometer was tested by studying the isochromatic surface at 200 kV [5]. Here, we study the spectral performance of the new instrumentation. The obtained ELNES was compared with the near-edge X-ray absorption fine structure (NEXAFS) measured with an energy resolution of 0.08 eV, which is much higher than that of a (S)TEM EELS available nowadays. To explore the information limit, band-structure calculations are performed using the full potential augmented plane waves code WIEN97 providing site- and angular-momentum-projected DOS.

For this purpose, divanadium pentoxide (V_2O_5) is chosen for its challenging fine-structure at the V L_3 peak. V_2O_5 crystallises in an orthorhombic, weakly bonded layered structure, with vanadium being surrounded by six oxygen atoms forming a strongly distorted octahedron unit [6]. There are three different types of oxygen: the one-fold bonded vanadyl oxygen, O_V, the two-fold bonded bridging oxygen, O_b and the three-fold bonded chain oxygen O_c. We have chosen the normal direction of the layer as c-axis.

Experimental and calculations

The high-energy resolution spectrum was recorded on a FEI TECNAI with a Wien filter monochromator, an improved high tension tank and a high-resolution GIF (HR-GIF) at the Centre for HREM at Delft University, The Netherlands. The electron optical energy resolution on the HR-GIF amounts to 40 meV using a 2 mm entrance aperture, and the resolution of the system can be tuned between 0.10 and 0.50 eV, depending on the requirements of the experiment [7]. The present measurement was done at a total energy resolution of about 0.22 eV, determined by measuring the FWHM of the zero-loss speak (Fig. 1). The recording time was 32 sec. The same experiment was repeated without monochromator (0.6 eV energy resolution) on the FEI TECNAI with the HR-GIF at the Graz University of Technology. For comparison with spectra from a 'common' instrument, spectra were also recorded on a Philips CM 200 FEG TEM using the GATAN GIF 200 imaging filter (1 eV energy resolution). V_2O_5 single crystals were used. The scattering geometry was arranged such that the incident electron beam is parallel to the **c**-axis. The X-ray absorption spectrum (XAS) was recorded at the undulator beam line

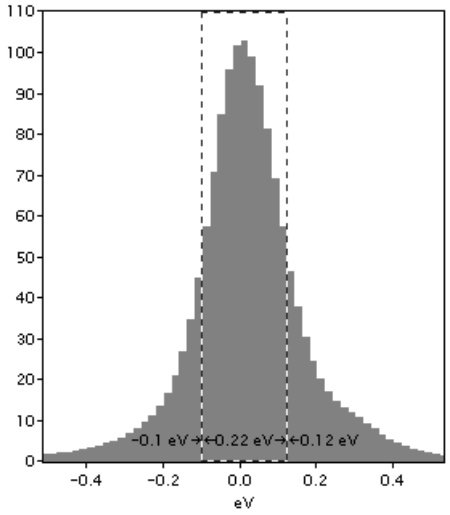

Fig. 1 The zero loss peak acquired on the Delft FEI TECNAI with a Wien filter monochromator, an improved high tension tank and a high-resolution GIF (HR-GIF). Recording time: 32 s.

UE/56-2 PGM-1 of the third generation synchrotron radiation facility BESSY in Berlin [8]. The polarisation vector **E** is perpendicular to the **c**-axis. The data were collected in the total electron yield mode under vacuum conditions. V_2O_5 single crystal was fixed on an alumina sample holder by a double adhesive conductive tape. The details of the band-structure calculation using the full potential augmented plane waves code WIEN97 have been published elsewhere [9].

Results and discussions

Fig. 2 shows the processed ELNES of V_2O_5, obtained with three energy-resolutions. Measurement with 1.0

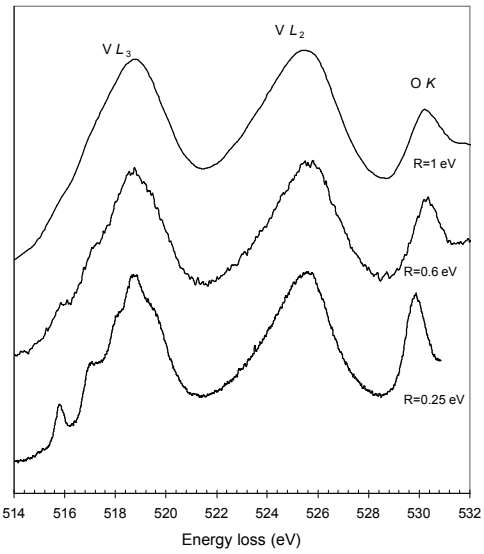

Fig. 2 ELNES of V_2O_5 measured with an energy resolution of 1, 0.6 and 0.22 eV respectively.

eV energy resolution provides only the basic shape of the V $L_{2,3}$ edge, with an edge maximum at 519 eV (V L_3) and 526 eV (V L_2), and the t_{2g}* peak of the O *K*-edge with the maximum at above 530 eV. Increasing the energy resolution, fine structure appears on the ELNES. Since the instrumental broadening decreases, the V L_2 edge and t_{2g}* peak of O *K*-edge become narrow as the energy resolution increases. Because of this narrowing the t_{2g}* peak increases in height. Moreover, due to the improved separation between V L_2 edge and the O-K t_{2g}* peak, the peak position of the O-K t_{2g}* shifts by about 0.6 eV to lower energy-loss. However, the great improvement is mirrored on the V L_3-edge: most fine spectral features are only clearly observable with the optimised spectrometer, where the monochromatised TEM exhibits a significantly better resolution of the edge structure (the peak at 515.8 eV, the plateau at 517.5 eV and the shoulders at 518.7 and 520.5 eV). It is clear that just reducing the energy resolution from 1 to 0.6 eV is not sufficient to resolve the fine structure on V L_3 edges.

Fig. 3 shows an enlarged diagram of the V L_3 edge fine structures measured with the 0.22 eV energy resolution

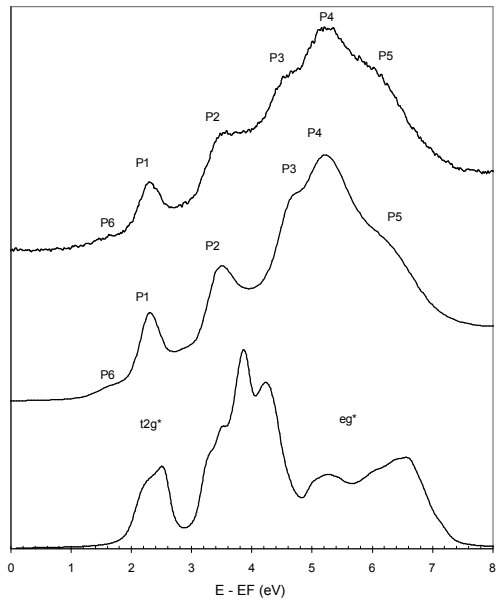

Fig. 3 V L_3-edge of V_2O_5 measured with an energy resolution of 0.22 eV (EELS, upper one) and 0.08 eV (XAS). The V L_3 ELNES calculated with the procedure described in [9] is added (lower curve).

and the V L_3 NEXAFS with an energy resolution of 0.08 eV. Due to the higher resolution, the plateau on ELNES at 517.5 eV turns into the resolved peak P_2 on NEXAFS. Also the mentioned two shoulders on ELNES become more apparent on NEXAFS. However, XAS, despite its fantastic energy-resolution of 0.08 eV, does not reveal any new feature in V L_3 NEXAFS than in V L_3 ELNES obtained with an energy-resolution of 0.22 eV. The collection angle for the acquisition of the EELS spectra was about 7.5 mrad and therefore small enough to ensure that the dipole selection rule applies (the dipole selection rule is valid for $\mathbf{q}.\mathbf{r}\ll 1$ where **q** is the momentum transfer and **r** the average radius of the overlap between initial and final states [1]). The density of unoccupied states in V_2O_5 is strongly dominated by the V 3d states which are dipole allowed final states for the V L_{23} edge [10]. The structures in the V L_{23} edge can therefore be interpreted in terms of V d DOS. We display the calculated V L_3 ELNES and folded with a Gaussian of 0.08 eV FWHM in Fig. 2. In the V 3*d* band the unoccupied t_{2g}* and e_g* states are almost completely separated at 4.7 eV above the Fermi level [9]. The t_{2g}* states appear in the energy range between 1.8 and 4.7 eV and e_g* states above that. One feature of the t_{2g}* state in the V 3*d* band is, due to the V $3d_{xy}$ – Oc $2p_x/2p_y$ hybridization, the 0.8 eV split-off at 2.4 eV above the Fermi level [10]. Fig.3 shows that the P_1 and P_2 features in ELNES and NEXAFS are due to the split-off of the V 3*d* conduction band; the estimated splits are 1.1 eV (NEXFAS) and 1.2 eV (ELNES). This is in good agreement with the calculated value of 1 eV, after being folded with a Gaussian of 0.08 eV FWHM. The plateau-like distribution of e_g* states in V 3*d* conduction band is concentrated in the region of 4.5 to 7 eV, with two edges 5 and 6.5 eV. These observations can be the explanation of the features P_4 and P_5 in ELNES and NEXAFS, although the matching of curves is not satisfying. According to the band-structure calculation, the feature P_6 at 1.5 eV in NEXAFS, which is very weak in ELNES, cannot be assigned to any transition to the unoccupied states in the V 3*d* conduction band. This feature could be due to surface states that are not considered in the present band-structure calculation. The present band-structure calculation does not allow the interpretation of the nature of P_3 feature on ELNES/NEXAFS. It seems that the rapid technical improvement in recording high-resolution ELNES at nanometer scale challenges the more precious solid-state calculations including core-hole effects and multiplet splitting.

Summary

We summarise this short report with the answers to the two questions formulated in the introduction: (i) the combination of the new spectrometer and the monochromised FEG TEM provides excellent data. Even with a total energy-resolution of 0.22 eV, the obtained ELNES is nearly comparable with NEXAFS data of 0.08 eV energy-resolution. (ii) The TEM/EELS with improved energy reso-

lution gives access to the same information as the synchrotron. This opens the exciting possibility to study the electronic structure of materials with the same physical method either in a surface-sensitive (XAS) or in a bulk sensitive (EELS) mode with complete geometric structure information (SAED, HREM) and nanometer lateral resolution. We expect a direct comparison of ELNES to DOS on the projected atom site in the near future. It should be noticed that improving the energy resolution is not always necessary: some physical effects like the core-hole and lifetime of excited states broaden the spectral features on one hand; some edges have simply broader structures (like the O-K edge in vanadium oxides). Another exciting possible application of HR-EELS is the investigation of the band gap region of semiconducting materials where information about electronic states could be directly related to structural informations obtained from TEM images and diffraction patterns.

Acknowledgement

The work at FHI is supported by the Deutsche Forschungsgemeinschaft SFB 546. The work at the FELMI-ZFE is supported by the Forschungsförderungsfonds der Gewerblichen Wirtschaft. The work at Delft University is supported by Stichting voor Fundamenteel Onderzoek der Materie (FOM).

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