

# A new approach to study bonding anisotropy with EELS

G.A. Botton\*

*Department of Materials Science and Engineering, Brockhouse Institute for Materials Research, McMaster University,  
1280 Main Street West, Hamilton, Ont., Canada L8S 4M1*

Received 15 January 2004; received in revised form 20 September 2004; accepted 20 September 2004

Available online 8 December 2004

## Abstract

A novel method to study the anisotropy of electron scattering is presented. The technique makes use of the two-dimensional capabilities of energy filters in transmission electron microscopes to study the energy-filtered scattering patterns obtained at different energy losses near ionization edges. The technique is demonstrated for the C–K edge in pyrolytic graphite at energy losses corresponding to the continuum background prior to the C–K edge, the unoccupied  $\pi^*$  and  $\sigma^*$  transitions and the continuum after the near-edge fine structure. The distribution of scattering for transitions to unoccupied  $\pi^*$  and  $\sigma^*$  electronic states is remarkably different as expected from experiments using the conventional techniques. The fine structure of the scattering distribution demonstrated with this approach, however reveals additional details that can be explained by the broader angular extent of the  $\sigma$ -orbitals between carbon atoms. Good agreement between the one-dimensional profiles extracted from the two-dimensional data and scattering models is observed.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** EELS; K-edge; Electron scattering; Chemical bonds

## 1. Introduction

The anisotropy in the physical properties of some solids is a reflection of their inherent anisotropic electronic structure. A variety of spectroscopic techniques can be used to investigate the anisotropy of the electronic structure of solids including angular resolved photoemission, inverse photoemission and orientation-dependent X-ray absorption spectroscopy. These techniques are surface sensitive and hence require great care in sample preparation and ultra-high vacuum so that contamination does not interfere with the measurements. Electron energy loss spectroscopy in the electron microscope is potentially an alternative technique that is increasingly becoming a more common tool to investigate at high spatial resolution the electronic structure of solids [1–3]. The two principal reasons for the growing interest in these techniques are the instrumentation developments that have made spectrometers and energy filters accessible to a large

materials science and physics community and the better understanding of fine structure at the characteristic core edges. The use of electronic structure calculations to understand EELS spectra has also evolved significantly in recent years so that spectra have been used to probe details of the bonding of materials so as to understand electronic structure features and the density of electronic states [4–8]. More recently, major developments have been made in the area of commercial instrumentation that have led to the use of monochromators and high-resolution energy filters in the transmission electron microscope [9–11]. This new capability makes it possible to obtain high-quality spectra with an energy resolution of about 0.1 eV that can be comparable to good X-ray absorption spectra. Such improvements combined with developments in aberration correctors [12–14] will lead to major breakthroughs in materials research.

At the fundamental level, when characteristic ionization edges are probed in an energy loss experiment, fast incident electrons excite core level electrons to unoccupied states and the resulting modulations at the edge threshold mostly reflect features in these unoccupied states. The unoccupied fi-

\* Tel.: +1 905 525 9140; fax: +1 905 521 2773.

E-mail address: [gbotton@mcmaster.ca](mailto:gbotton@mcmaster.ca).

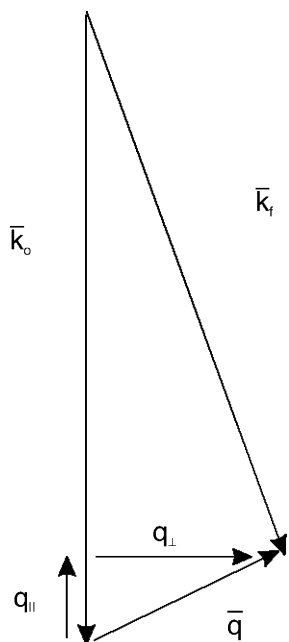


Fig. 1. Scattering diagram for the energy loss event.  $\vec{k}_o$  and  $\vec{k}_f$  are the incident and scattered wave vectors,  $\vec{q}$  is the scattering vector.

nal states are not all equally probed since the transition selection rules must be respected. Transitions are thus allowed when the change in angular momentum quantum number is  $\Delta\ell = \pm 1$ . For example, when an electron from an initial 1s state is excited (as for K-edges), transitions will only occur to 2p states; when the initial level is 2p (as for L-edges) the final states will be 3s and 3d. The observed spectra directly represent the unoccupied electronic states with various degrees of modification of the features due to the excitation effects. For example, simple transition metal oxides, nitrides and carbides such as TiO, TiO<sub>2</sub>, NiO, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, TiN and TiC [6,15] can be fully described by a single-particle description of the unoccupied electronic states directly obtained from density functional theory calculation. Other materials such as GaN, AlN, MgO and Al<sub>2</sub>O<sub>3</sub> require the introduction of core-hole effects into the calculations that lead to different degrees of success [8,16–18].

In addition to the energy loss event, there is a significant momentum transfer between the interacting electrons. In the conventional acquisition of energy loss spectra for chemical microanalysis and, for most purposes, in near-edge fine structure analysis, the momentum transfer to the incident electrons is averaged out over a large collection angle of the aperture of the spectrometer. The momentum transfer to the ejected electron causes a non-negligible scattering angle (Fig. 1) and can lead to an angular dependence of core edges in particular collection conditions. These effects can be controlled with a series of measurements and minimized by using the recently developed “magic-angle” technique [19,20] that allows to average out angular dependent measurements into one single spectrum. This technique makes it possible to compare the fine structure of materials that have anisotropic crystalline

structures but otherwise would be similar (e.g. disordered versus highly-oriented pyrolytic graphite). This technique can also be used to retrieve the independent angular components from a series of controlled measurements. The flexibility in the control of the momentum transfer demonstrated in these measurement methods with EELS is one of the most significant differences with XAS as the momentum transfer with photons is negligible. Even if the momentum transfer and the induced scattering angle are often disregarded or averaged out in routine spectral acquisition these quantities are, in principle, potential parameters that can be varied during the experiment in the electron microscope when this instrument is operated in diffraction mode. The pioneering work of Leapman et al. [21] showed that it is possible to obtain energy loss spectra showing the orientation dependence of core edges in the case of C–K edge in graphite and in boron nitride. The technique has been applied since then to superconductors in dedicated spectrometers (e.g. Ref. [22,23]) which offer very limited spatial resolution (in the order of 0.3 mm) and conventional microscopes [24,25] with few tens of nanometers resolution. The orientation dependence of EELS spectra has been exploited with substantial modifications to the original technique proposed by Leapman et al. [21] in the high resolution scanning electron microscope for the study of defective graphite [26], and magnetic materials [27] with near-nanometer resolution. The approach suggested by Leapman et al. [21] gives a full spectrum or a series of spectra at selected scattering angles and hence orientations (typically two spectra for two mutually perpendicular transitions (say parallel and perpendicular to the *c*-axis when hexagonal crystals are used) and does not fully allow to explore the details of the transition probabilities for a large portion of reciprocal space or several directions in the crystalline structure.

With the advent of energy filters fitted to transmission electron microscopes, new possibilities are available as energy selected diffraction patterns can be readily obtained. In addition to elemental mapping to find out the distribution of elements in a sample, these energy filters have been used so far to filter out all inelastic contributions in diffraction patterns of relatively thick specimens in order to carry out work in quantitative electron diffraction [28–32]. However, the momentum transfer information for selected energy losses is also a parameter that can be exploited with these instruments. When the energy loss representative of a particular transition is chosen with an energy-selecting slit of the energy filter, the transition probability distribution in momentum space can be visualized.

This paper describes the first implementation of the method and its application to the test case of graphite. The study focuses on the carbon K-edge which represents electronic transitions, caused by the fast incident electrons interacting with atoms in the sample, from 1s ground states to 2p unoccupied final states. The results show that the anisotropy of this system is readily visualized and that the scattering angle probability distribution significantly varies with the selected energy loss. Transitions to unoccupied  $\pi^*$  and  $\sigma^*$  or-

Download English Version:

<https://daneshyari.com/en/article/9585212>

Download Persian Version:

<https://daneshyari.com/article/9585212>

[Daneshyari.com](https://daneshyari.com)