Excitonic, vibrational, and van der Waals interactions in electron energy loss spectroscopy

T. Mizoguchi [a,*], T. Miyata [a], W. Olovsson [b]

[a] *Institute of Industrial Science, University of Tokyo, Tokyo 153-8505, Japan*
[b] *Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden*

ARTICLE INFO

ABSTRACT

The pioneer, Ondrej L. Krivanek, and his collaborators have opened up many frontiers for the electron energy loss spectroscopy (EELS), and they have demonstrated new potentials of the EELS method for investigating materials. Here, inspired by those achievements, we show further potentials of EELS based on the results of theoretical calculations, that is excitonic and van der Waals (vdW) interactions, as well as vibrational information of materials. Concerning the excitonic interactions, we highlight the importance of the two-particle calculation to reproduce the low energy-loss near-edge structure (ELNES), the Na-$L_{2,3}$ edge of NaI and the Li-K edge of LiCl and $LiFePO_4$. Furthermore, an unusually strong excitonic interaction at the O-K edge of perovskite oxides, $SrTiO_3$ and $LaAlO_3$, is shown. The effect of the vdW interaction in the ELNES is also investigated, and we observe that the magnitude of the vdW effect is approximately 0.1 eV in the case of the ELNES from a solid and liquid, whereas its effect is almost negligible in the case of the ELNES from the gaseous phase owing to the long inter-molecular distance. In addition to the "static" information, the influence of the "dynamic" behavior of atoms in materials to EELS is also investigated. We show that measurements of the infrared spectrum are possible by using a modern monochromator system. Furthermore, an estimation of the atomic vibration in core-loss ELNES is also presented. We show the acquisition of vibrational information using the ELNES of liquid methanol and acetic acid, solid Al_2O_3, and oxygen gas.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Electron energy loss spectroscopy (EELS) observed with transmission electron microscopy (TEM) has been extensively used in diverse fields, such as materials science, solid state physics, biological chemistry, and polymer chemistry [1]. The reason for this wide range of applications is attributed to the numerous advantages of the TEM-EELS method. The most important advantage is its high spatial resolution. EELS observation with very high spatial resolution has been achieved more than twenty years ago by the combination of EELS with a scanning transmission electron microscope (STEM) [2–5]. To date, some milestones for the atomic resolution analysis using STEM have been recorded by a pioneer, Ondrej L. Krivanek, and his collaborators and the instruments developed by them [6–11]. In 2010, the ultimate resolution, that is atom-by-atom analysis, was achieved [11].

In addition to the spatial resolution, the wide variety of information obtainable from an EELS spectrum is also an important ad-

vantage of the EELS method. Information on the chemical composition of a sample can be obtained by from the fine-structure of its core-loss EEL spectrum. The spectral profile and threshold energy of ELNES are known to be sensitive to the local coordination, valence state, and chemical bonding. A lower energy profile of the EELS spectrum also contains important information on the material. The low loss profile originates from phonons, collective electron oscillations, as well as the inter and intra band transitions, and thus, optical properties can be measured using low loss EELS [1,12]. With a modern aberration-corrected STEM system, atomic resolution observation of the spectrum from a single dopant [9], two-dimensional mapping of elements in a bulk [13] and at a interface [14], dopant buried in a crystal [15], and valence state mapping [16], are all possible. Some of these cutting-edge observations have been performed by the instruments developed by the group of Krivanek and coworkers [9,14].

Furthermore, new techniques in EELS have also been developed recently. The observation of magnetic circular dichroism using ELNES has been achieved using a vortex electron beam [17–19]. More recently, an improvement of the energy resolution, via the development of an advanced monochromator system, enables

* Corresponding author.
E-mail address: teru@iis.u-tokyo.ac.jp (T. Mizoguchi).

the identification of fine profiles near the zero-loss peak [20–23], as described in a review [24]. An instrument that is compatible for both advanced spatial resolution and energy resolution has also been developed by Krivanek et al. [25–27]. The advanced energy resolution enables us to provide information on the electronic structure at the band gap (gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) and the vibration of atoms in the molecule and solid [25,28,29].

Nowadays, the TEM/STEM-EELS method is a very informative and powerful analytical technique for a wide variety of scientific fields. Significant pioneering contributions were made by Ondrej L. Krivanek to open up these frontiers, as described above. Based on this background, we would like to show further potential applications of EELS, based on the results of theoretical calculations. In this study, we discuss 1) excitonic interactions in ELNES, 2) effect of van der Waals interactions in ELNES, and 3) vibrational information from EELS.

The excitonic interaction is known to be significant in ELNES in the relatively lower energy region, <100 eV [30–35], whereas its effect on the high energy ELNES is still a cause of controversy [32,36]. We have investigated the excitonic interactions in the low energy ELNES, Na-$L_{2,3}$ edge ($\sim$30 eV) of NaI and the Li-K edge ($\sim$50 eV) of LiCl [37], as well as the high energy ELNES at the O-K edge ($\sim$530 eV) of perovskite oxides [36]. Here, we review those results, and an application of the excitonic calculation is also shown for the Li-K edge and Fe-$M_{2,3}$ edge of a Li-ion battery cathode material, LiFePO$_4$, and the importance of correct calculation of the transition energy is demonstrated.

Concerning the van der Waals (vdW) interaction, it is known that one of its constituents, the London dispersion force, can be estimated from the plasmon loss [38]. However, the effect of the vdW interaction in core loss, ELNES, has not been discussed. We have investigated the effect of the vdW interaction on the B-K edge of solid h-BN, the O-K edge of liquid water, and the O-K edge of a gas water molecule using first-principles calculations [39].

In addition to the above "static" information, we investigated the "dynamic" behavior of atoms in materials, such as phonons and molecular vibrations, in the EELS spectrum. Direct observation of the vibrational spectrum using monochromated STEM-EELS from an ionic liquid, C$_2$mim-TFSI, has been reported [29]. Furthermore, we have also reported the effects of the molecular vibration on the liquid ELNES, C-K edge of liquid methanol and O-K edge of acetic acid [40,41]. Here, in addition to those previous results, we show the effect of the lattice/molecular vibration on the Al-K edge of solid Al$_2$O$_3$ and O-K edge of oxygen gas.

2. Excitonic interactions in ELNES

The features of ELNES originate from an electron transition from a core-orbital to the conduction bands. Here, the "ground state" is defined as the state before the electron transitions and the state with a core-hole is called an "excited state". At the excited state, a Coulombic interaction between the positively charged core-hole and the negatively charged excited electron, namely an excitonic interaction, is present.

To investigate the excitonic interaction, a correct calculation of the two-particle formalism, namely the Bethe–Salpeter equation (BSE), is necessary [30,31,33,34]. The method to calculate the excitonic interaction using BSE is provided next.

2.1. Methodology for the excitonic calculation

To investigate the excitonic interaction, both the one-particle and two-particle calculations were performed. In the one-particle

calculations, the electron-hole interaction is treated under the generalized gradient approximation (DFT-GGA). Namely, the particle–particle interactions are approximated to be interactions between an electron and the mean field generated by other particles. Hereafter, we will name the one-particle calculation as "DFT-GGA". In DFT-GGA, one core-hole is introduced into the respective core-orbital, and the electronic structure at the excited state is calculated. To minimize the artificial interactions between core-holes, a large supercell was used. The theoretical transition energy was also calculated in the one-particle calculation by the total energy difference between the excited state and ground state [35].

In the two-particle calculation, the BSE calculation was performed to accurately consider the two-particle (electron–hole) interactions. The effective two-particle Hamiltonian with spin-orbit interaction, which treats the excitonic effect, is described as:

$$H^{eh} = H^{diag} + H^{dir} + H^x, \tag{1}$$

where H^{diag}, H^{dir}, and H^x are the diagonal term, the direct term, and the exchange term, respectively [31].

To calculate the BSE, the one-particle wave functions obtained from the DFT-GGA calculation were used in this study. Hereafter, we will name the two-particle calculation "BSE-GGA". However, this BSE-GGA method has a disadvantage in that it cannot estimate the theoretical transition energy [42]. A correct estimation of the theoretical transition energy becomes important when a spectrum is overlapped or very close to another spectrum. For instance, the Li-K edge of Li-ion battery cathode materials always encounters this problem. The cathode materials usually include both Li and 3d transition metals (TM), and the position of the Li-K edge and the TM-$M_{2,3}$ edge are very similar. In such a case, the theoretical transition energy must be estimated separately using the DFT-GGA method.

In the present study, we used suitable calculation codes depending on the purpose. First-principles all-electron calculation codes based on the augmented plane wave and local orbital (APW+lo) method, WIEN2k code [43], and a full-potential linearized augmented plane wave (FLAPW) method, and the Elk code were used for the one-particle calculations [43,44]. All the BSE-GGA calculations were performed using the Elk code. To correctly calculate the spectra, the size of the supercell, number of k-points, and the cutoff energy of the plane wave were carefully chosen.

2.2. Low energy ELNES

The excitonic interaction is known to be significant for a relatively lower energy ELNES, because the core-hole and the excited electron are energetically and spatially close to each other. For instance, the Li-K and Na-$L_{2,3}$ edges appear around 50 eV and 30 eV, respectively, and thus, the excitonic interaction is expected to be significant. To show the strong excitonic interaction in the low energy ELNES, the Na-$L_{2,3}$ edge of NaI and Li-K edge of NaCl were investigated.

The Na-$L_{2,3}$ edges of NaI are shown in the Fig. 1(a). The experimental spectrum was determined using X-rays in a previous report [45]. As can be seen in the figure, the experimental spectrum shows an intense excitonic peak B which is followed by a small peak, a relatively intense peak, and a plateau profile. These characteristic features appear in both the BSE-GGA and DFT-GGA calculations. Furthermore, the small splitting in peak B can only be reproduced when spin–orbit coupling is considered. However, a detailed investigation shows that the position of peak B is overestimated by DFT-GGA. However, the BSE-GGA calculations correctly reproduced the position. A similar overestimation of the excitonic peak position with DFT-GGA has also been observed for the Li-K edge of Li compounds [35]. The experimental and calculated Li-K edge of LiCl are also shown in Fig. 1(b). The calculated spectra us-