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Low-energy electron energy losses and inelastic mean free paths in zinc, selenium, and zinc selenide

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A B S T R A C T

We compute low-energy optical energy loss spectra for the elemental solids zinc and selenium, and for the binary compound zinc selenide. The optical data are transformed via a constrained partial-pole algorithm to produce momentum-dependent electron energy loss spectra and electron inelastic mean free paths. This enables a comparison between the electron scattering behaviour in a compound solid and its constituent elements. Results cannot be explained by aggregation methods or commonly used universal curves, and prove that new approaches are required. Our work demonstrates new capabilities for the determination of fundamental material properties for a range of structures previously inaccessible to established theoretical models, and at energy levels inaccessible to most experimental techniques.

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1. Introduction

The electron inelastic mean free path (IMFP) is one of the most fundamental parameters describing electron transport in a material. It defines the mean distance travelled by an electron between successive inelastic collisions, and is crucial for quantitative analysis of a variety of spectroscopic and imaging tools such as electron energy loss spectroscopy (EELS), auger electron spectroscopy (AES), elastic peak electron spectroscopy (EPES), and electron microscopy. A strong body of literature exists, particularly from the last 35 years, following the development of theoretical models used in the determination of IMFPs in elemental solids [1–4], and tabulations are available across a broad energy range, typically from 50 eV to 30 keV [5].

Recent experimental work, however, has raised questions about the accuracy of these tabulations in the low energy regime, particularly below around 120 eV [6–8]. Few tabulations quote any data at all below 50 eV – an important region dominated by plasmon excitations that has particularly significant effects on structural analysis tools such as X-ray absorption fine structure (XAFS) analysis [9] and low energy electron diffraction (LEED) [10]. Further, information regarding IMFPs in compound structures generally must be inferred from elemental tables following universal curves or aggregation techniques [11].

These problems are largely due to difficulties in accurately quantifying the optical energy loss function (ELF) for a material in the low energy region. The ELF may be interpreted physically as the relative probability of a material accepting an electronic excitation with a given energy $\hbar\omega$ and momentum $\hbar q$, and is expressed in terms of the complex dielectric function $\epsilon(q, \omega) = \epsilon_1(q, \omega) + i\epsilon_2(q, \omega)$ following

$$\text{ELF} = \text{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right] = \frac{\epsilon_2(q,\omega)}{\epsilon_1(q,\omega)^2 + \epsilon_2(q,\omega)^2} \tag{1}$$

This quantity is not to be confused with the energy loss spectrum, which describes the response of the incoming particle, rather than the response of the absorbing/scattering material. The ELF is said to be the optical ELF in the limit $q \to 0$, due to the small momentum supplied by a photon relative to an energetic electron. Modern theories, including the full Penn algorithm [5], partial pole models [12], and self-energy/Green's function approaches [13] all rely on transforms of the optical ELF in order to estimate the IMFP.

Optical ELF data used in IMFP calculations have previously been sourced almost exclusively from experimental data, with the optical transmission and reflection measurements of Hagemann et al. [14] and the exhaustive compilation of Palik [15] being most commonly cited. In recent times REELS measurements have also provided experimental optical ELFs, which have sometimes shown significant disagreements with the aforementioned tabulated data [16].

These tabulations are often inconsistent, do not typically provide uncertainties, and do not generally cover all elemental solids, let alone any useful range of compounds. It is therefore

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essential that a theoretical framework be defined in order to provide a generalised approach to optical ELF, and subsequent IMFP, determination. We have made developments in the application of density functional theory (DFT), which enables calculations of a range of optical properties at low excitation energies for periodic systems [16]. In this work we utilise those developments in a study of the binary compound zinc selenide, enabling not only the first ever published determination of the IMFP of ZnSe, but also an analysis of the relationship between the optical and electron energy loss properties of a binary material and those of its constituent elements. This allows us to critically investigate longstanding assumptions regarding the aggregation of IMFPs for compounds and mixtures, and demonstrates the value of a purely theoretical approach for the detailed study of a more general class of materials.

2. Theory

The optical dielectric function for a material with complex band structure, such as a periodic solid, is commonly expressed as a summation of terms corresponding to the dielectric response of an ensemble of nearly-free electron gases. The basic theory for the quantum-mechanical free-electron gas is given by Lindhard [17]. One can utilise Lindhard dielectric functions to construct the solid-state optical dielectric function following [18]

$$\epsilon(0,\omega) = 1 + \lim_{q\to 0} \frac{4\pi e^2}{q^2} \sum_{n,n',\mathbf{k}} \frac{f^0(\mathbf{k}) - f^0(\mathbf{k+q})}{E_{n'}(\mathbf{k+q}) - E_n(\mathbf{k}) - \hbar\omega} |M_{n,n'}(\mathbf{k},\mathbf{q})|^2 \quad (2)$$

where the Lindhard expressions, characterised in terms of the Fermi distribution f_0, are modulated by a series of transition matrix elements $M_{n,n'}(k,q)$. These terms can be expressed approximately as

$$M_{n',n}(\mathbf{k},\mathbf{q}) = \langle n', \mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|n, \mathbf{k+q}\rangle \quad (3)$$

The detailed procedure for the evaluation of Eq. (2) has been developed by Ambrosch-Draxl and Sofo [18] and implemented into a module for the band structure package WIEN2k [19]. WIEN2k utilises a self-consistent field algorithm to determine electron eigenstates $|n, \mathbf{k}\rangle$ for periodic structures following a linearised augmented plane-wave (LAPW) implementation of Kohn–Sham DFT. The Kohn–Sham equation is given by

$$\left(-\frac{\hbar}{2m}\nabla^2 + V_{Ne} + V_{ee} + V_{xc}\right)\psi = E\psi \quad (4)$$

where the potential components correspond to the nuclear–electron interactions (V_{Ne}), electron–electron interactions (V_{ee}), and exchange and correlation (V_{xc}). These components can be evaluated as functions of local electron densities, alleviating the need for consideration of pair-wise electron interactions – an intractable problem for a solid.

With this framework in place one can determine the optical dielectric function $\epsilon(0, \omega)$ and consequently the optical ELF Im$[-1/(\epsilon(0, \omega))]$. As mentioned, the transformation of the optical ELF is critical for the evaluation of the electron IMFP. Here we utilise a partial pole transformation [12], which utilises the natural q-dependence of the Lindhard theory to obtain the momentum-dependent ELF Im$[-1/(\epsilon(q, \omega))]$. To wit:

$$\text{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right] = \sum_i A_i \text{Im}\left[\frac{-1}{\epsilon_L(q,\omega;\omega_p = \omega_i)}\right] \quad (5)$$

where $\epsilon_L(q, \omega)$ is the Lindhard dielectric function. The principal defining parameter for a Lindhard function is the plasma frequency ω_p which, in the partial pole model, may take on a number of values ω_i resulting from the different local free-electron gas densities

that are considered to make up the scattering material. The relative amplitudes of the Lindhard terms at different plasma frequencies are given as A_i, and these may be evaluated using the requirement that the momentum-dependent ELF matches that calculated in the optical limit via DFT:

$$\text{Im}\left[\frac{-1}{\epsilon_{\text{DFT}}(0,\omega)}\right] = \sum_i A_i \text{Im}\left[\frac{-1}{\epsilon_L(0,\omega;\omega_p = \omega_i)}\right] \quad (6)$$

Since the Lindhard dielectric function leads to delta function components in the optical ELF, this criterion is straightforward to fulfil by allocating closely spaced, periodic ω_i values and defining the amplitude parameters A_i following

$$\text{Im}\left[\frac{-1}{\epsilon_{\text{DFT}}(0,\omega)}\right] = \sum_i \frac{A_i \pi}{2\omega}\delta(\omega - \omega_i) \quad (7)$$

This enables us to build a complete electron ELF Im$[-1/(\epsilon(q, \omega))]$. Recalling that this function is interpreted physically as a relative probability of an excitation occurring in the scattering material, we express the electron IMFP in terms of the ELF following the well-known relation [3]:

$$\lambda^{-1}(E) = \frac{\hbar}{a_0 \pi E} \int_0^{((E-E_F)/\hbar)} \int_{q_-}^{q_+} \frac{1}{q}\text{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right] dq\, d\omega \quad (8)$$

The limits of integration for the momentum transfer, $q_\pm$, are given by

$$q_\pm = \sqrt{\frac{2mE}{\hbar^2}} \pm \sqrt{\frac{2m}{\hbar^2}(E - \hbar\omega)} \quad (9)$$

following kinematic requirements with respect to the energy transfer of the incoming electron.

3. Results

We first examine, in Fig. 1, the optical ELFs determined via DFT for zinc, selenium, and zinc selenide. We note that the optical response of solids is often highly dependent on the crystal or molecular structure, and that the crystal systems of these three materials - hexagonal for zinc, trigonal for (grey) selenium, and cubic zincblende for zinc selenide – are highly varied.

Despite these variations, we are surprised to find that the optical ELF of ZnSe is qualitatively representative of an aggregate of the responses of Zn and Se. Specifically, while the main feature of the Zn loss function is a clear double-peak at 13 eV and 19 eV, and the Se spectrum exhibits a well-defined single peak at 20 eV, the ZnSe
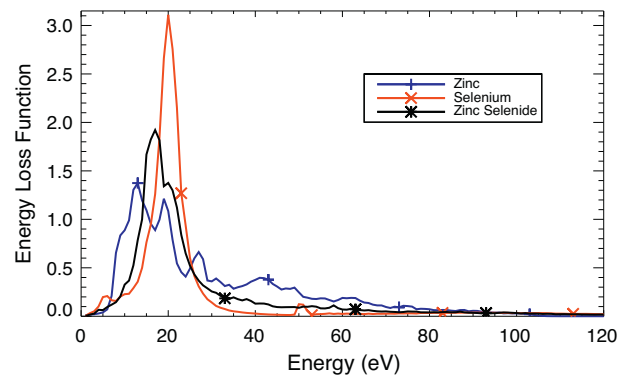

Fig. 1. Optical energy loss functions of zinc, selenium, and zinc selenide determined using the WIEN2k implementation of density functional theory. Despite substantial structural differences between the three materials, the major peak of ZnSe is qualitatively similar to the aggregate heights, widths, and energy positions of the major peaks associated with its component elements.