Microsc. Microanal. Microstruct. **2** (1991) 153–158 APRIL/JUIN **1991**, PAGE 153

Classification
Physics Abstracts
78.70Dm — 71.70b — 79.20Kz

Theoretical description of near edge EELS and XAS spectra

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(Received February 08, 1991; accepted March 26, 1991)

Abstract. — In this communication I want to briefly describe the contents of the talk I presented at the lake Tahoe EELS conference. Since most of what I talked about has or will appear in print in another form, I will restrict myself to very brief descriptions of in my view relevant basic ideas and supply a list of references in which more details can be found.

First of all it is important to recognize the similarities and differences between high energy electron energy loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS). If we neglect the exchange terms in EELS the differential cross-section for energy loss is given by [1]

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E} - \frac{\hbar^2}{(\pi e a_0)^2}\frac{1}{q^2}\mathrm{Im}\left[-\frac{1}{\epsilon(q,\omega)}\right]$$

where $\epsilon(q,w)$ is the dielectric function and q is the scattering vector of the incident high energy electrons. We will be dealing with core level spectroscopy and the near edge structure for which Re $\epsilon(q,\omega)\sim 1$ and IM $\epsilon(q,\omega) << 1$ and

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E} \propto |<f|\mathrm{e}^{-iq\cdot r}|i>|^2\delta\left(\hbar\omega - E_\mathrm{f} + E_\mathrm{i}\right) \simeq |<f|\mathbf{q}\cdot\mathbf{r}|i>|^2\delta\left(\hbar\omega - E_\mathrm{f} + E_\mathrm{i}\right)$$

which describes transitions from an initial state Ψ_i to a final state Ψ_f which now involve the excitation of a core electron to the valence band. For high incident energies and small q the result is similar to that of optical absorption (XAS)

$$\sigma(\mathrm{XAS}) \propto |<f|\varepsilon\cdot\mathbf{r}|i>|^2\delta\left(\hbar\omega - E_\mathrm{f} + E_\mathrm{i}\right)$$

where the scattering vector q in EELS plays the role of the polarization vector of the light ϵ in XAS.

The differences lie primarily in the different characteristics of an electron and a photon beam.

a) EELS incident energy can be chosen and at high energy is less surface sensitive than XAS
b) $|q|$ can be varied in EELS changing selection scales from dipole to quadrupole and allowing

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$\Delta S \neq 0$ transitions via the exchange terms.

c) An electron source can be easily focused to a very small region (atomic resolution)

d) XAS causes less radiation damage in general and can be applied to bulk crystals whereas EELS is limited to thin films

e) Photons can be circularly polarized which is interesting for magnetic circular dichroism.

We will limit ourselves to dipole selection rules keeping in mind the possibilities of looking at dipole forbidden transitions with EELS. The dipole selection rules are $\Delta L = \pm 1$, $\Delta S = 0$ or $\Delta J = \pm 1, 0$ where ΔL, ΔS and ΔJ are the orbital, spin and total angular momenta changes between initial and final states. This means that the choice of the core electron state determines the character of the valence states which can be studied. s→p, p→d or s, d→f or p etc. For solids this allows the determination of the local symmetry projected partial density of states in cases where the core hole potential itself does not have a dominating influence. Utilizing also the polarization dependence we have selection rules; ϵ along $Z \rightarrow \Delta m_J = 0$ $\epsilon \perp Z$ $\Delta m_J = \pm 1$ for linearly polarized radiation and in XAS $\Delta m_J = +1$ for right circularly polarized light and $\Delta m_J = -1$ for left circularly polarized light where Δm_J is the change in the magnetic quantum number. With linear polarized light (or as in EELS) we can probe details of the local symmetry. For example for ϵ // Z only the p_z partial density of states is probed in a K edge experiment. This has been used in many adsorbate systems as well as the high T_c superconductors. With circular polarized light one can probe the local magnetic moment and study magnetic field dependencies since the spectra for $\Delta m_J = +1$ and $\Delta m_J = -1$ are different only if time reversal symmetry is broken. The effects observable with linear and circular polarization have recently been elegantly described by Carra and Altarelli [2].

Core level spectroscopy.

Core holes have a fairly short lifetime yielding a line width ≥ 0.1 eV. A review of some core level linewidths has been published by Fuggle and Alvarado [3]. Some of these results should be regarded as upper limits since broadening due to multiplet structures have not been separated from lifetime effects in all cases [4,5]. These lifetimes are short compared to any delocalization time of the core hole so the core is hole localized at a particular site making the technique site selective and a **local** probe.

The XAS (EELS) spectrum involving a core level is usually separated into three regions depending on the energy from threshold (E_{th});

$E - E_{\text{th}} \geq 100$ eV EXAFS - measure local structure around the core hole site

$E - E_{\text{th}} \approx 5$ to 50 eV XANES - measure the local symmetry projected density of conduction band states.

$E - E_{\text{th}} \leq 5$ eV Edge Structure - measure details of local electronic structure involving multiplets, crystal field, magnetic moments, etc.

I will concentrate on the details of the edge structure and discuss the information we can obtain from such studies.

It is instructive to consider two extreme situations for the valence band states. States for which the radial extent of the free atom wave function is large or comparable to the interatomic spacing in the solids $R \geq d$ and states for which $R << d$. The s, p bands of metals as well as 6d bands of the rare earths fall under $R \geq d$. These states are well described by band theory. The 3d states of transition metal compounds and the 4f states of rare earths fall in the category $R << d$. For $R << d$ the on-site Coulomb Interactions are large and often comparable to band widths so that correlation effects are of utmost importance. These states support local magnetic moments and the electronic structure is well described by a renormalization atom or ion approach in which the translational symmetry is of secondary importance. By renormalized I mean to take into account proper point group symmetries and screened interactions. These states behave like "core" states but they are of great importance for the physical properties because they are not "closed shell". Sometimes these atomic like highly correlated states coexist and hybridize with s, p, d bands where $R \geq d$ leading phenomena like the Kondo effect. A more detailed description can be found in references [6,7,8]. The reason why this separation is interesting for XAS (EELS) is not only because of the strongly different ground state properties but also because the core hole valence electron interaction can be classified in the same way. This interaction will be weak compared to valence electron band widths for $R \geq d$ and will be strong compared to band widths for $R << d$. We therefore expect that for transitions to states for which $R \geq d$, the effect of the core hole is small so that the local symmetry projected local density of states is measured. If, however, the transitions are to states for which $R << d$ core hole excitons with the atomic multiplet structure will be observed. Much of the work involving core level spectroscopies has been reviewed recently [9].

We now come to examples of core level XAS (EELS) spectra and their interpretation in terms of the valence band electronic structure. I choose to divide this discussion into three parts consistent with the above classification. We start with unoccupied states with only $R \geq d$ states of importance. The K edges of simple metals like Al, Mg then probe the local p density of states which are modified only little by the core hole potential. The core hole potential effect here is significant only in the threshold singularity behaviour. A little further ~1 eV from threshold the spectra can be compared to band structure calculation and provided matrix elements are taken into account properly, the agreement is often quite reasonable except for very interesting shifts especially at higher energies ~10-15 eV above threshold due to energy dependent self-energy effects. Since the spectra probe the local symmetry projected density of states XAS can be used to sort out the various contributions from different orbitals and different sites in, for example, an alloy to the total unoccupied density of states. For example, the Al K edge in Al Ni alloy yields the Al 2p contribution to the unoccupied density of states [10].

The next category discussed involves intermediate cases. These are cases in which the core hole potential and/or the exchange interaction with the valence electrons is smaller than but comparable to the valence band width. There are basically two types of core-valence interactions, the monopole Coulomb interaction given by the Slater F^0 integral and the interactions which result in multiplet structure F^2, G^1, G^3 etc. which include also exchange types of integrals (G's). F^0 is strongly screened in solids (even in insulators) reduced from ~18 eV to ~6-8 eV for the Cu 2p-3d interaction. The exchange and orbital dependent terms are not or hardly screened [11].

To get a feeling for orders of magnitude the $2p^5 3d^1$ configuration of say Sc has a multiplet spread of about 3 eV of which 2 eV is due to exchange. The 3d band width is about 5 eV and the 2p spin orbit splitting is ~7 eV. Such intermediate cases can only be handled properly for initially **empty** d bands like say Ca or Sc and to some approximation Ti. Provided we can assume an empty *d* band to start with, then the various interactions described above can be treated on an equal footing. These types of calculations have been done for Ca, Sc, Ti [12] and the main parts of experimental observations have been explained [13]. Some of these observations were

a) the strong deviation from the statistical intensity ratio of the L_3 and L_2 edges
b) the strong difference between observed spectra and the calculated density of states
c) the delayed onset due to exchange interaction.

Up to now only the nearly empty band systems can be treated in this way. However as shown by Thole and van der Laan [14] the L_3/L_2 intensity ratio can also for the heavier 3d transition metal yield quite direct information about the importance of 3d spin orbit coupling in the ground state.

A third category involves systems with strong core level-valence interactions. These types of materials like the 3d transition metal compounds as well as rare earth compounds are well known for the strong satellites observed in core level XPS measurements [15,16]. The lowest binding energy component often called the well screened line involves a valence electron configuration with an extra electron (as compared to the ground state) in a localized $R << d$ orbital like a 4f for rare earths or a 3d orbital for the transition metals. This is the lowest energy final core hole state because of the very strong attractive interaction between a core hole and a 4f or 3d electron. The satellite corresponds to a poorly screened state in which the valence orbital occupation is the same as that of the ground state. For XAS things are a bit different depending on the choice of the core hole state. For a core hole state such that a transition to the screening orbital is not dipole allowed (for example the K edges of transition metal compounds or $L_{2,3}$ edges of the rare earths) we expect a very complicated structure which might be roughly approximated by a convolution of the XPS spectrum with the valence band local density of states of $\ell + 1$ character [17,18].

If the core hole is chosen so that a transition to the screening orbital is optically allowed we go directly to the screened final state and for a large core hole potential very narrow spectra exhibiting atomic like multiplet structure are expected and observed [19,20]. The rare earth M_{45} spectra for example exhibit a rich multiplet structure which is a direct fingerprint of the ground state spin and orbital angular momentum [20].

The 3d transition metal 2p edges show again a rich multiplet structure [19], which in the compounds, clearly shows the lowering of local point group symmetry from the free atoms. From the spectra detailed information can be obtained concerning the local symmetry, the crystal field splittings, the local spin and the importance of the spin orbit coupling [21-24].

For the 3d transition metal oxides it is also interesting to look at the OK edge [25] or the C or NK edges in carbides and nitrides [26]. Such transitions form a class in its own because although the empty valence states are of 3d character ($R << d$) the interatomic interaction of these with the O core hole is negligibly small. The reason that such transitions have intensity at all is because of the covalent mixing between the TM 3d orbitals and the ligand p orbitals. Recent studies of NiO have demonstrated that the intensity is a direct measure of the covalency in the ground state [27]. Such studies can provide also quite direct measure of crystal field splittings [25]. For substituted materials like $Ni_{1-x}Li_xO$ [27] and the high T_c superconductors [28,29] the character of the holes introduced by substitution can be determined. It is from these studies that the important conclusion that the holes are primarily in the O 2p orbitals has been drawn.

The last subject I want to touch upon concerns the polarization dependent studies. As is clear from the discussion above one can with linear polarized radiation or q dependent EELS determine the orientation of empty states. For example, OK edge data can identify if the empty O 2p states are of p_x, p_y or p_z symmetry. For the high T_c's they are of primarily p_x or p_y i.e. $\perp$ to the c axis symmetry [28,30]. Also transitions from say Cu 2p states to Cu $3d_{x^2-y^2}$ states are not allowed for z polarized radiation making the identification of the symmetry of empty states possible [31].

The use of linear or circular polarized radiation can also be used to study the ground state magnetic properties of magnetic materials. Perhaps it sounds a bit strange but even with a resolution of only 0.5 eV one can in rare earths determine the Zeeman splittings of the states which are less than 10 meV with magnetic X-ray dichroism [32-34]. The magnetic dichroism for transitions from core levels like TM 2p or rare earth 3d to respectively the strongly screening orbitals TM 3d or rare earths 4f can be extremely strong (up to 100%). Even in Ni metal strong effects are observed which provide direct information on the orbital part of the magnetic moment in the ground state [35]. Using circularly polarized light Schütz *et al.* [36,37] have also observed significant MXD for $L_{2,3}$ core levels in the rare earths for which transitions are not into the screening orbitals but rather into the broad valence d bands. From these studies the authors demonstrate that one can determine the exchange splitting of the bands in ferromagnetic materials.

In conclusion, I have provided some references in which the theory and some experiments of core edge XAS structures are described. We have found that

a) for broad band systems XAS and EELS measure primarily the $\ell + 1$ local projected density of states for a core state of orbital angular momentum ℓ;

b) for intermediate to strong interactions with the core hole only a few cases can be solved theoretically. Information, can be obtained about the orbital moment in the ground state from for example the L_3/L_2 intensity ratio;

c) for strong interaction with the core hole we expect and observe multiplets which are a fingerprint of the details of the ground state like, J, L, S, α (seniority no.) as well as local crystal field symmetry and splitting;

c) polarization dependent measurements yield the local symmetry of the empty states. For magnetically ordered materials the local (site selective) magnetic moment, and its temperature and field dependence can be determined.

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