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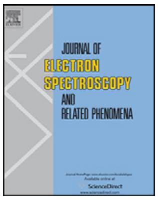

Review

The iron L edges: Fe 2p X-ray absorption and electron energy loss spectroscopy

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ABSTRACT

The iron L edges are reviewed. The experimental spectra obtained with 2p XAS, XMCD and 2p EELS are discussed, including isolated iron atoms, solids and coordination compounds. The largest fraction of publications deal with iron oxide systems that are discussed in detail, including binary oxides, perovskites and spinel systems. Emphasis is given on fundamental studies that focus on spectral shape analysis. We have selected a number of applications for further discussion, including iron in astrochemistry, iron complexes and nanostructures in catalysis, iron in mineralogy, the pnictide superconductors, spin cross-over systems and phthalocyanine and related systems.

Some of the important theoretical concepts in the analysis of L edges are discussed, including atomic multiplet theory, crystal field theory, charge transfer theory and XMCD. The 2p XAS spectra contain much detail for halides, oxides and coordination compounds. These spectra can be analyzed in great detail, revealing much information, including the valence, the spin state and the crystal field parameters. Covalent compounds and metal alloys have spectra with much less detail, which makes analysis more difficult.

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1. Introduction

This review discusses the iron 2p X-ray absorption spectroscopy (XAS) and Electron Energy Loss Spectroscopy (EELS) spectra of iron materials. In L edge X-ray absorption, a 2p core electron is excited to an empty state. The binding energy of the 2p core state of iron is approximately 710 eV. This implies that L edge XAS spectra are excited with 710 eV soft X-rays using one of the soft X-ray beamlines at a synchrotron light source. The EELS spectra are measured with electron microscopes using a primary energy of typically 80–200 keV electron energy.

This review focuses on spectral shape analysis of the L edges. We will not discuss the experimental aspects in detail and refer to papers dedicated to this topic. We assume XAS and EELS to measure an identical spectrum given by the dipole transition operator. The iron L edge XAS spectrum can be measured in transmission mode, but given the short probing depth of 710 eV photons this is only possible for thin samples. For example, transmission X-ray microscopy (TXM) is measured in transmission mode [77]. The majority of soft XAS spectra are measured with electron yield detection or fluorescence yield detection. Yield methods detect the decay of the core hole, which gives rise to electrons and X-rays escaping from the surface of the substrate. This allows the measurement of samples with arbitrary thickness. The large interaction of electrons with matter implies that the electrons that escape from the sample originate close to the surface and the probing depth of electron yield methods is approximately 2–5 nm. The fluorescent decay of the core hole can also be used as the basis for the XAS measurement, but only for dilute systems.

In Section 2, we discuss the 2p XAS spectrum of a free iron atom, allowing the description of the spectral shape to be limited to a single atom in spherical symmetry. Section 3 discusses ionic solids and section 4 focuses on iron oxides. Section 5 deals with covalent solids such as sulphides and metal alloys. Section 6 deals with coordination compounds, including proteins.

2. Atoms and ions

We start the discussion of the 2p XAS spectra of iron systems with an isolated iron atom. This allows us to explain some of the fundamental issues concerning L edges, in particular the importance of intra-atomic interactions such as the 3d3d interactions, the 2p3d interactions and the 2p and 3d spin–orbit coupling.

An isolated iron atom has an electronic configuration $3d^6 4s^2$. The ground state configuration of the six 3d electrons is given by the Hunds rule. All five spin-up states are filled and the sixth electron fills the spin-down state with $m_l = +2$. This yields a ground state with $L = 2$ and $S = 2$, represented by a ^5D term symbol. The ^5D state is split into five substates by the 3d spin–orbit coupling and because the 3d shell is more than half full, the ground state has $^5D_4$ symmetry. The ground state is split into states with have, from low to high energy, the J quantum number equal to respectively 4, 3, 2, 1 and 0. The 2p X-ray absorption spectrum can be calculated by performing an atomic multiplet calculation of the final state in which a 2p electron has been excited to a 3d state, which corresponds to a $2p^5 3d^7 4s^2$ configuration. The 2p spin–orbit coupling is large and splits the spectrum into its L_3 and L_2 components. The 2p3d multiplet interaction, in other words the higher order interaction of the electron–electron repulsion term coupling the 2p and 3d electronic states, is also large. The result is a large number of atomic states. Fig. 1 shows that atomic multiplet calculation for the transition $3d^6 \rightarrow 2p^5 3d^7$ for the five different J-states of the ^5D ground state symmetry. The relative energies of the J-states with respect to the $J = 4$ ground state are respectively 54 meV ($J = 3$), 92 meV ($J = 2$), 116 meV ($J = 1$) and 128 meV ($J = 0$).

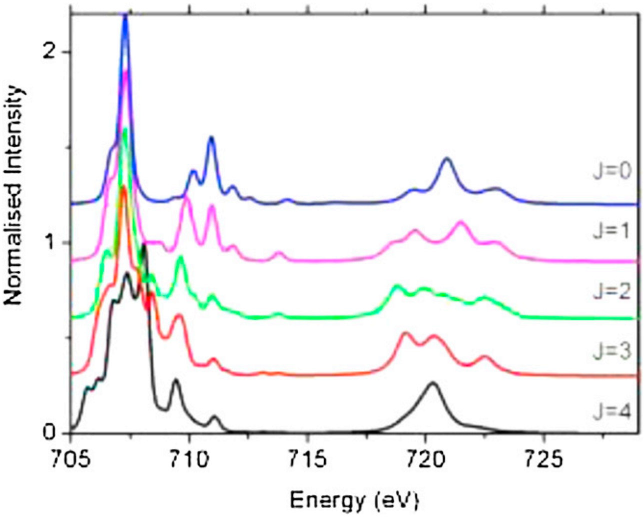

Fig. 1. the atomic multiplet calculations for the five different J-states of the ^5D ground state for the $3d^6 \rightarrow 2p^5 3d^7$ transition.

The theoretical spectra have been compared with the experimental 2p XAS spectrum of an iron atom [196,225]. The experimental spectrum has been measured in electron yield mode at 1750 K. Because of this high temperature, one should calculate a Boltzmann distribution over the different J substates. Fig. 2 shows the experimental 2p XAS spectrum of an iron atom, compared with the $J = 4$ ground state, the spectrum calculated without 3d spin–orbit coupling and the spectrum derived from a Boltzmann distribution at 1750 K. It can be observed that the 1750 K spectrum reproduces the experiment, including the features at the leading edge. This experimental spectrum, as well as the 2p XAS spectra of the other transition metal ions has been measured and calculated by Martins et al. [196].

The 2p XAS spectrum of a single iron atom on a potassium surface has been measured by Gambardella et al. [97]. They also measured the X-ray magnetic circular dichroism spectrum (XMCD), the difference between left and right polarized X-rays for a magnetized sample. Fig. 3 shows the 2p XAS spectra for Fe^{1-} ($3d^7 4s^2$), Fe^0/Fe^{2+} ($3d^6 4s^2/3d^6$) and Fe^{3+} ($3d^5$). The spectra for Fe^{2+} are equivalent to those of an iron atom (Fe^0) because the 4s electrons do not modify the spectral shape. Both Fe^0 and Fe^{2+} have a $^5D_4$ ground