Electronic structure of ilmenite: X-ray absorption and DFT study

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Abstract. The experimental Ti K-edge X-ray absorption near edge structure (XANES) spectrum of the mineral ilmenite was recorded. The theoretical Ti K-XANES spectra of ilmenite were simulated using both the self-consistent real-space full-multiple scattering theory within the muffin-tin approximation for the potential shape and the full-potential finite difference method. The comparison of the theoretical spectra with the experimental XANES is discussed. The electronic structure of ilmenite was investigated by analyzing the distribution of the partial densities of electron states.

1. Introduction
Titanium is an element that is widely distributed in the Earth's crust and mantle. It is a component of a number of minerals, including ilmenite (FeTiO3). Ilmenite is an economically important mineral, which is named after its place of discovery in the Ilmen Mountains (Russia). It has also been found in lunar rocks and some meteorites. Investigations of ilmenite from cosmic bodies have been widely described [1-3], such as the ilmenite-bearing basaltic Martian meteorite, Los Angeles [1].

Ilmenite can often contain appreciable amounts of manganese and magnesium, so the full chemical formula can be stated as (Fe,Mg,Mn,Ti)O3 [4-5]. The crystal structure and local atomic environment of ilmenite at different conditions has been studied by several techniques [6-7]. One of the most effective methods for investigating the local atomic structure and distribution of unoccupied electronic states is X-ray absorption spectroscopy (XAS). While Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy gives information about the coordination number and bond length around the absorbing atom, X-ray Absorption Near Edge Structure (XANES) spectroscopy can provide full information about local geometry including not only bond lengths but also the bond angles [8-9].

XANES spectroscopy has already been applied to the study of ilmenite. Experimental XANES spectra of both the titanium K-edge [10-12] and iron K-edge [11, 13-15] have been measured and analyzed. Experimental XANES spectra of the titanium L2,3 and iron L2,3-edges are discussed in [11]. But, to our knowledge, the theoretical Ti K-XANES spectra of ilmenite have not been reported in the literature.

The electronic structure of FeTiO3 has been studied previously (see, for example, [15-17]). The electronic, magnetic and structural properties of ilmenite were calculated using a hybrid density functional formalism [16]. The electronic structure of FeTiO3 was investigated on the basis of high resolution electron energy loss spectroscopy (EELS) combined with the theoretical multiplet calculations [17]. Mössbauer spectroscopy, XANES spectroscopy and DFT theory were also applied to
obtain the iron electronic oxidation state of FeTiO$_3$ at different pressures [15]. Magnetic structure of hemato-ilmenite was investigated in [18].

In the present paper we concentrate our attention on the X-ray absorption spectra near the Ti K-edge of ilmenite. The theoretical Ti K-edge XANES spectra calculated on the basis of both full multiple scattering and finite difference methods are analyzed and compared with the experimental data. We also provide an investigation of the electronic structure of ilmenite by computing the partial density of electronic states.

2. Experiment and method of calculation

X-ray absorption spectra near the titanium K-edge of the mineral ilmenite were recorded in fluorescence mode at the Australian National Beamline Facility; Beamline 20B (bending magnet) at the 2.5 GeV Photon Factory (KEK, Tsukuba, Japan). The spectral energy resolution was about 1.8 eV. XANES spectra were recorded from 4955–5200 eV, using a step size of 0.2 eV from 4955–5015 eV and 0.25 eV above 5015 eV.

Ti K-XANES spectra of ilmenite were calculated in the electric dipole approximation on the basis of both the real space full multiple scattering method within the FEFF8.4 program [19] and the full-potential finite difference theory implemented in the FDMNES2008 code [20].

The FEFF8.4 program allows \textit{ab initio} self-consistent full-multiple scattering calculations to be carried out. The approach uses the muffin-tin (MT) approximation for the shape of crystal potentials [21]. In the code there is a possibility to choose between several models for the exchange-correlation potential. In the present study test calculations have established that in the case of the Ti K-XANES of ilmenite the best agreement between the experimental and theoretical spectra is achieved using the Hedin-Lundqvist model for the potential. Calculations were done in ground state and in excited state taking into account the core hole created by electron transition. In the last case the electronic configuration of the absorber with only one 1s electron was taken into consideration.

In the FDMNES2008 program code the calculations used the non-self-consistent finite difference method. The advantage of the FDMNES2008 code as compared with the FEFF8.4 program is that FDMNES2008 allows the calculations to be carried out in so-called ‘full potential’ (beyond the MT approximation for the potential shape). The Hedin-Lundqvist model of exchange-correlation potential was used for XANES simulations.

Ground state partial densities of electronic states (pDOS) of ilmenite were calculated using the FEFF8.4 code.

All calculations in the present study used the structural data for FeTiO$_3$ from [22].

3. Results and discussion

As the first step of the investigation the Ti K-XANES spectrum of ilmenite was simulated on the basis of the real-space full multiple scattering theory (FMS) using the FEFF8.4 code. The first step in the FMS analysis is the determination of the minimum size of the atomic cluster around the central absorbing titanium atom, within which the scattering of the photoelectron can reproduce all fine structures of the experimental XANES spectrum. Thus, a comparison of the experimental Ti K-XANES spectrum with those calculated for clusters of different sizes (containing from 11 till 396 atoms) was performed. It was found that, in principle, all main features of the XANES spectrum were reproduced for a small cluster containing 48 atoms (the radius of the cluster is 5 Å). Increasing the size of the cluster only results in the insignificant redistribution of XANES peak intensities. The convergence of the XANES is observed for a cluster with a radius of about 9 Å, consisting of about 284 atoms. Further increasing of the size of the atomic cluster doesn’t lead to any changes in the XANES spectra including the intensity redistributions.

In figure 1 the comparison of the experimental Ti K-edge XANES spectrum of ilmenite with the theoretical spectra calculated using the FEFF8.4 program code for an atomic cluster of 284 atoms is presented. To investigate the influence of the core hole created by the electron transition on the shape of the Ti K-XANES ilmenite spectrum, the theoretical spectra were simulated with taking into account...
Figure 1. Comparison of the experimental Ti K-XANES of ilmenite with theoretical spectra calculated using the FMS method (FEFF8.4 code) and FDM theory (FDMNES2008 code). Theoretical spectra calculated taking the core hole into account are shown by solid lines, without it by dotted line. All spectra are aligned relative to the energy position of peak D of the experimental spectrum.

The core hole and without it (dotted line in figure 1). It can be seen that the core hole doesn’t influence significantly the shape of the Ti K-XANES spectrum of ilmenite. A comparison of the experimental and theoretical data (figure 1), indicates that the theoretical XANES calculated using FEFF8.4 agree quite well with the experimental spectrum in the energy position of peaks $B$, $C$, $D$ and $E$, but the energy position of peak $F$ is a little bit overestimated. The energy of the pre-edge feature marked by $A$ also disagrees with the experimental results.

Next, the Ti K-edge XANES of ilmenite was simulated on the basis of the full-potential finite difference method (FDM) using the FDMNES2008 program. As XANES spectra simulated using FDM theory, in principle, converge faster with increasing the cluster size than those calculated using the FMS method, we carried out the XANES simulation using the FDMNES code for a cluster with a radius of 7 Å containing 135 atoms. The theoretical spectrum obtained taking the core hole into account is also shown in figure 1. The XANES calculated using the FDMNES code results in agreement with the experimental energy position of features $A$, $B$, $C$, $D$ and $E$, but, on the other hand, the position of the maximum $F$ is underestimated.

Figure 2. Partial densities of the electronic states (DOS) of ilmenite. The Fe $d$-DOS, Ti $d$-DOS, O $p$-DOS are divided by 8, 8 and 10, respectively. The origin of the energy scale corresponds to the zero of the muffin-tin potential. Approximate position of Fermi energy is -11.6 eV. Dotted curve in figure 1 corresponds to Ti $p$-states multiplied by dipole transition matrix element [23].

Summarizing the analysis and comparing the two methods of simulating XANES spectra – FMS
within the MT approximation (implemented within the FEFF8.4 program) and full-potential FDM (realized in the FDMNES2008 code), one can conclude that the overall agreement between the theoretical and experimental XANES is better with FDM.

To study the electronic structure of ilmenite the pDOS near the top of the valence band as well as near the bottom of the conduction band were simulated for atomic cluster of radius of 9 Å (284 atoms). The obtained pDOS are presented in figure 2 and their analysis shows that the bottom of the conduction band of ilmenite is formed by Ti-\(d\) and O-\(p\) states with some admixture of the Fe-\(d\) states, while the top of the valence band is formed by Fe-\(d\) states and (at lower energy) O-\(p\) states.

4. Conclusions

In the present work the experimental Ti K-XANES spectrum of ilmenite was compared with theoretical spectra simulated using two approaches – real-space full multiple scattering theory within the MT approximation for the potential shape (FEFF8.4 program) and the full-potential finite difference method (FDMNES2008 code). It was found that both methods result in good agreement between the theoretical and experimental data, but, nevertheless, the overall agreement between the theoretical and experimental XANES is better with FDM. The distribution of the partial densities of the electron states of ilmenite was also analyzed.

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