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Comparison of Mg L_{23} edges in MgO and $Mg(OH)_2$—Importance of medium-range structure

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ABSTRACT

Mg L_{23}-edge electron energy-loss near-edge structure in $Mg(OH)_2$ was studied experimentally and theoretically for comparison with that of MgO. The differences in the near-edge fine structure between $Mg(OH)_2$ and MgO were interpreted as a result of differences in medium-range structure.

1. Introduction

Absorption near-edge fine structures, in both electron-loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS), carry both structural and chemical information on materials. In principle, an absorption spectrum is due to quantum-mechanical transitions that excite a particular inner-shell electron of a specific atom to the unoccupied states, i.e. to states with an excited electron above the Fermi energy, leaving behind a core hole. Therefore, absorption intensities are determined by transition rates, which are governed by the Fermi's "golden rule" in terms of a squared transition matrix times a density of states (DOS) for available energy states [1–3]. According to multiple scattering (MS) theory, the outgoing excited electron can be considered as a quantum electron wave that spreads out over the material [4]. The surrounding atoms can be divided into shells and act as scattering centers, which scatter the outgoing electron wave back towards the original atom. The amplitudes of the outgoing electron wave and all the reflected waves add up at the absorbing atom either constructively or destructively, and hence modulate the matrix element between the initial and final states [4]. Due to the limited lifetime of the excited electron, the excited electron state decays rapidly as a function of time and distance. Therefore, absorption fine structure is only sensitive to the local atomic structure and chemistry (or composition) over a very short range, typically on an order of several nanometers or less [5]. In some cases, the local atomic arrangement (i.e. coordination) is more dominant in deriving the near-edge fine structure than the local chemistry, and thus the so-called "fingerprint" technique can be used in identifying site occupation or coordination of a given element in different compounds [6,7].

The success of the "fingerprint" approach relies on a robust relationship between near-edge fine structure and atomic local structure or other physical and chemical properties, such as valence state. In other words, fine structure in EELS should be deduced directly from the local atomic structure or other properties without need of theoretical calculations. In reality, however, this is almost impossible; the successful cases where this robustness exists are rare [8]. Slight distortions within the first nearest neighbors may not alter the near-edge fine structures significantly, but a short bond length can certainly do so [9]. In addition, medium-range order may also change the near-edge fine structure [10]. Recently, it has been argued that delocalization in fine structure (due to the finite range of the ejected core electron) should also be added to the delocalization of inelastic scattering (due to the finite impact parameter of the beam electron) when high spatial resolution is required in measurements [11]. In this paper, we compare the experimental Mg L_{23} energy-loss near-edge fine structure (ELNES) between $Mg(OH)_2$ and MgO. The differences between these spectra are found and the interpretation is given as the result of their medium-range structures.

Although it has been shown experimentally and theoretically that Mg L_{23} edges are very unlike each other in octahedral (e.g. MgO) and tetrahedral (e.g. $MgAl_2O_4$) coordinations [12–14], significant differences also exist in Mg L_{23} and K-edges in the same coordination compounds. Mg atoms are all in octahedral coordination in both $Mg(OH)_2$ and MgO, and the Mg–O bond lengths are also similar in these two compounds: they are 2.10

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and 2.09 Å in $Mg(OH)_2$ and MgO, respectively. However, the Mg K-edge in $Mg(OH)_2$ is dominated by one-peak feature, while it has two distinctive peaks in MgO [15,16]. An interpretation of the differences in the Mg K-edge between $Mg(OH)_2$ and MgO has not been given in the literature.

From a structural point of view, the differences between MgO and $Mg(OH)_2$ involve both short- and long-range order. In the short-range order [17], the Mg coordination is a perfect octahedron in MgO, while it is a distorted one in $Mg(OH)_2$, as shown in Fig. 1. In addition, Mg^{2+} is surrounded by O^{2-} in the former, while it is octahedrally coordinated by hydroxyl groups in the latter. In the long-range order, $Mg(OH)_2$ consists of two sheets of hydroxyls parallel to the basal plane and a sheet of Mg ions between these hydroxyls which are in hexagonal close packing with each other of the hydroxyls linked to three Mg on the one side and fitted into three hydroxyls of the next layer. The Mg octahedra share adjacent edges to form sheets of layers. On the other hand, MgO has a NaCl-type three-dimensional structure. The difference in their short- and long-range orders automatically results in their different structures in the medium-range order. As predicted by the MS theory, the long-range periodic order may not be responsible for the difference in the near-edge fine structure of absorption edges in these compounds, but the differences in local structure (both in short- and medium-range order) and local chemistry may be. Here we aim to understand why the absorption near-edge fine structures are so different between $Mg(OH)_2$ and MgO.

2. Experimental and theoretical methods

$Mg(OH)_2$ crystals were used in this study (Aldrich Chemical Company, Inc.). MgO samples were obtained by thermal dehydration of $Mg(OH)_2$ at 1000 °C for 2 h in air. The transmission electron microscope (TEM) specimens were prepared by grinding the samples into powders in acetone, and picking them up using a Cu grid covered with a lacy carbon thin film. The sample was then immediately transferred into and observed in a JEOL 2010 TEM with a field-emission gun operating at 200 keV and a Gatan's Enfina parallel EELS spectrometer. It was known that the electron beam could cause dehydration in $Mg(OH)_2$ directly [18]. Therefore, in order to exclude any radiation damage effect the Mg L_{23}-edge EELS spectra of $Mg(OH)_2$ were acquired under low beam intensity in the fashion of *in situ* observations, in which the time-dependent change of spectra were monitored [19]. (By contrast, MgO is relatively stable under electron beam.) The readout beam intensity at the small screen was ~5 pA/cm^2 at magnification of 80,000. The beam was spread out, and thus the convergence angle can be ignored. The EELS spectra were acquired in diffraction mode. The collection semi-angle was about 5 mrad. The full-width at half-maximum (FWHM) of the zero-loss peak without specimen was about 1.0 eV. To reduce the noise from channel-to-channel gain variations of the photodiode, a series of spectra were acquired with each spectrum shifted prior to acquisition by 0.5 eV relative to the previous spectrum, which is not equal to the inter-diode spacing. The resulting spectra were realigned before being added together. The background intensities were fitted by the intensities prior to the absorption edges using power-law functions and subtracted from the original data.

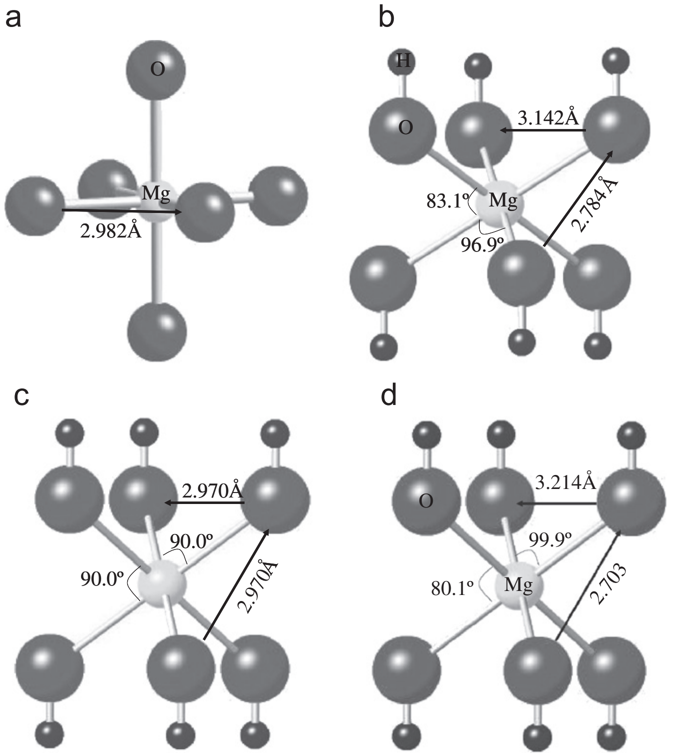

Fig. 1. The nearest-neighbor structures around Mg in (a) MgO, (b) $Mg(OH)_2$, (c) modified $Mg(OH)_2$-I, and (d) $Mg(OH)_2$-II. The structure parameters are given in Table 1.

The simulations of Mg L_{23}-edge EELS were carried out using Code FEFF8, which is based on real-space full-MS theory [20,21]. In brief, the method takes into account MS of the excited core electron by the surrounding atoms, which are divided into shells and the scattering calculated by including a successively large number of shells. Self-consistent muffin-tin (MT) potentials were used in the calculations. The MT radii are 1.05, 1.36 and 0.83 Å for O, Mg and H, respectively, with about 10% overlap to roughly correct for nonspherical potentials. The core-hole effect was included in the calculations using the "final state" approximation, i.e. an electron was removed from the Mg $2p_{2/3}$ orbital.

For comparison, the calculations were also carried out using the full potential linearized augment plane wave plus local orbital method, as encoded in the WIEN2K program [22]. For the exchange-correlation potential, the generalized gradient approximation (GGA) [23] was employed. MT radii of 1.21 for O, 1.97 for Mg and 0.65 (au) for H were used. In order to simulate core-hole effects, $2 \times 2 \times 2$ super-cells were constructed for both $Mg(OH)_2$ and MgO and the excited Mg atom in the super-cell treated as an impurity, of which a core electron was removed from the Mg $2p_{2/3}$ orbital and placed in the valence band.

Experimental lattice parameters and atom positions of $Mg(OH)_2$ [24] and MgO were used, without further relaxation in the calculations. The structure parameters are listed in Table 1.

Table 1
A list of structure parameters for MgO and $Mg(OH)_2$

	MgO	$Mg(OH)_2$	$Mg(OH)_2$-I	$Mg(OH)_2$-II
	$Fm\bar{3}m$ $a = 4.213$ Å Mg (0, 0, 0) O (0.5, 0.5, 0.5)	$P\bar{3}m1$ $a = 3.142$ Å $c = 4.766$ Å Mg (0, 0, 0) $O(\frac{1}{3}, \frac{2}{3}, 0.2216)$ $H(\frac{1}{3}, \frac{2}{3}, 0.4303)$	$P\bar{3}m1$ $a = 2.970$ Å $c = 4.504$ Å Mg (0, 0, 0) $O(\frac{1}{3}, \frac{2}{3}, 0.2692)$ $H(\frac{1}{3}, \frac{2}{3}, 0.4799)$	$P\bar{3}m1$ $a = 3.214$ Å $c = 4.875$ Å Mg (0, 0, 0) $O(\frac{1}{3}, \frac{2}{3}, 0.2016)$ $H(\frac{1}{3}, \frac{2}{3}, 0.4103)$
Mg–O	2.109 Å	2.100 Å	2.100 Å	2.100 Å
O–Mg–O	90°	83.1° 96.9°	90°	80.1° 99.9°

The modified structure parameters of $Mg(OH)_2$ are also given in this table.