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(Fisica, chimica, geologia, paleontologia e mineralogia)

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Fisica e Mineralogia. — *Synchrotron radiation XANES spectra for oxygen and magnesium in MgO (periclase).* Nota di IVAN DAVOLI (*), ELEONORA PARIS (**) e ANNIBALE MOTTANA (*), presentata (****) dal Corrisp. A. MOTTANA.

ABSTRACT - The X-ray absorption edges for O and Mg in MgO(periclase) have been measured using the GS line of PULS at ADONE synchrotron facility. With the available set-up, the edge for Mg (in the energy range 75 to 100 eV) is very blurred due to an exceedingly low signal to background ratio. However, the O edge (in the 520 to 580 eV range) is rather well resolved. The edge occurs at 543.5 eV and is followed by a main feature at 562.0 eV (± 0.5 eV). In addition, two weak features at 553.2 and ≈ 556 eV and a shoulder at ≈ 573 are present. XANES results are discussed on the basis of the known NaCl-type structure of periclase: the edge features are related to second-shell interaction effects.

KEY WORDS: XANES; Periclase; Magnesium; X-ray edge; Synchrotron.

RIASSUNTO. - *Spettri XANES per ossigeno e magnesio del periclasio (MgO).* Le soglie d'assorbimento a raggi X dell'ossigeno e del magnesio nel MgO (periclasio) sono state determinate con la linea GS del PULS del sincrotrone ADONE di Frascati. Nelle condizioni sperimentali usate, la soglia del MgZ(che si trova nell'intervallo energetico tra 75 e 100 eV) è molto debole; ciò è dovuto a un rapporto di conteggio sfavorevole tra picco e fondo. Invece la soglia dell'ossigeno (che si trova nell'intervallo 520-580 eV) è ben risolta. Oltre alla soglia p.d. a 543,5 eV, essa mostra un massimo a 562,0 eV (± 0,5 eV), due deboli oscillazioni a 553,2 e 566 eV, una spalla a circa 573 eV. Le sue irregolarità sono spiegate con effetti di interazione nel secondo strato di coordinazione. Il suo significato viene discusso in riferimento alla struttura nota, tipo salgemma, del periclasio.

INTRODUCTION

X-ray near edge spectrometry (XANES), the extension to lower energy of the well-known EXAFS technique, has become increasingly popular among material

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scientists as a technique suitable for examining the electronic structure of solid phases. The same popularity has not been attained yet among mineralogists, despite the fact that XANES gives information on local coordination, oxidation state, degree of covalency, and stereochemical variation around the excited atom (cf. Calas *et al.*, 1984, and Davoli *et al.*, in press).

Most XANES work so far concerns heavy elements, the edges of which lie in the energy range excited via either conventional white X-ray sources or synchrotron light. Few studies concern light elements, as their absorption edges occur at very low energy; their measurement would require a cumbersome windowless set-up at the synchrotron source, as well as very long counting times.

In this paper, we report measurements of the absorption edges of Mg and O in periclase (MgO-Fm3m, containing 66.3 wt% Mg and 39.7 wt% 0). Both are light elements, never thus far examined because of the above-mentioned difficulties inherent in the experiment. Work on them has been carried out mainly by the EELS method (e.g. Lindner *et. al.*, 1986). To the best of our knowledge, only lately the O X-ray absorption edges of a variety of alkaline-earth and transition metal oxides have been measured using synchrotron radiation (Nakai *et al.*, 1987).

Experimental set-up

The XANES spectra were taken in the PULS laboratory at the ADONE synchrotron facility of INFN, Frascati, using the windowless GS line. For a description of the set-up, the reader is referred to Davoli *et al.* (in press); a full description of the GS line can be found in Chiaradia *et al.* (1986).

Experimental results

The determination of the absorption edge for Mg was attempted in the energy range 75 to 110 eV, typical of such an element (the theoretical L-edge of Mg is at 88.6 eV: Williams, 1986). The excitation obtained in this range is extremely low; consequently, despite the high Mg content of our sample, the features obtained are extremely ill-defined due to the low peak-to-background ratio. However, an asymmetric edge can still be observed, with maxima at about 79 and 88 eV. After the second maximum, the absorption by the sample increases up to the EXAFS portion of the spectrum.

The K-absorption edge of O occurs in the range 530 to 580 eV, (theoretically at 543.1 eV: Williams, 1986). In this range the excitation power of the ADONE synchrotron light is substantially greater, the peak-to-background ratio is definitely better, and a well-resolved asymmetric edge can be determined. The edge peak is located at 543.5 ($\pm$ 9.5 eV), and is followed by two small features at 553.2 and 555.8 eV, a major peak at 562.0 eV, and eventually a shoulder at about 573 eV (Fig. 1).

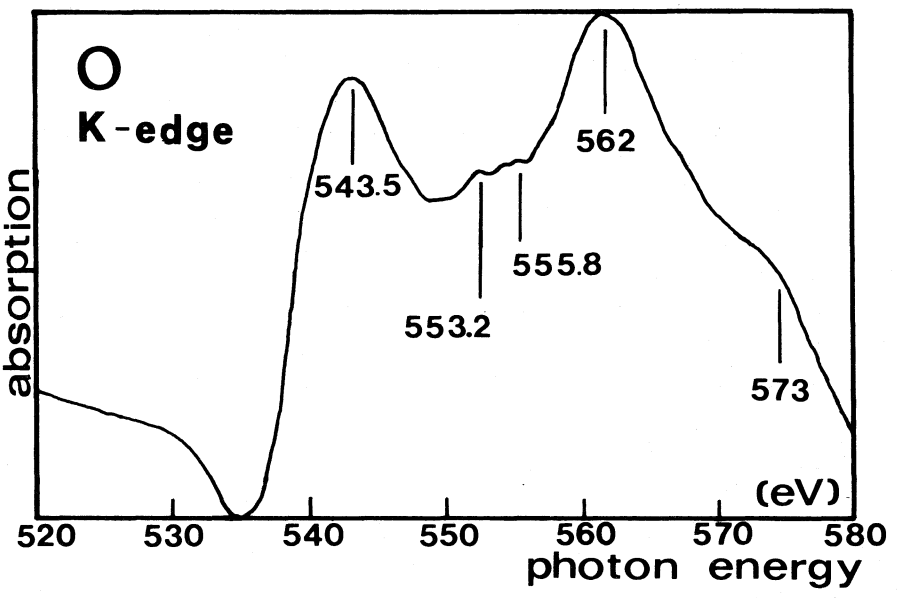

Fig. 1

The observed edge agrees with Nakai *et al.* (1987) one, but it is not as well resolved as theirs. As a matter of fact, our observed edge is broad enough as to allow us to infer that it averages the several fine structures detected by Nakai *et al.* On the other hand, our wider field of measurement allowed us to detect the second major peak at 562.0 eV, as well as to resolve the minor features at 553.2 and 55.8 eV, thus confirming some features of Lindner *et al.* (1986) spectrum which had been overlooked by Naki *et al.* in their 1987 synchrotron radiation experiments.

Discussion

Periclase has the halite structure, ideally consisting of a cubic-close-packed array of anions with the cations occupying the octahedral interstices. However, the sizes of O^{2-} and Mg^{2+} are such as to preclude such an ideal structure. In fact the oxygens are prevented from touching each other by the magnesium ions, the size of which is too large to be accomodated in the ideal array and forces it to expand. In addition, the difference in electronegativity suggests that the Mg-O bond is not purely ionic, but has some 25% of covalency. In spite of this, the electrostatic field around each ion is likely to be isotropic, as it also turns out from the application of both Pauling's second rule and Verwey-Heilman's maximal charge neutralization principle.

Having this structural model in mind, we shall now apply to the observed oxygen edge the semiclassical model describing physical radiation. Accordingly, a photoelectron, displaced from its orbital by the impinging synchrotron radiation, reaches the continuum only after undergoing multiple scattering processes.

The main edge at 543.5 eV is undoubtably due to interaction of the electron photo-emitted from O and the six Mg atoms surrounding it at a distance of 2.1006 Å. The two weak features at 553.2 and 555.8 eV most likely derive from interaction with O anions forming the second coordination shell of the absorbing atom. This interaction is made possible by the fact that Mg cations do not constitute a full shelter but actually leave «holes» of spherical triangular shape, through which the photoemitted electron can interact with the second shell oxygens. There are two possible kinds of interactions:

a) against the 8 oxygens forming the corners of two orthogonal squares around the central absorbing one, at a distance of 2.971 Å (in the ideal structure);

b) against other 8 oxygens, forming the corners of a cube, at the protracted distance of 3.638 Å.

The second possibility seems unlikely, as it implies far too large a difference in energy. The first possibility fits better the observed energy shift, but it implies a distortion around the site greater than expected from the structural model. In fact, Dell'Ariccia *et al.* (1984) formula permits to calculate that the eight O of the second coordination shell distribute more or less equally over two average distances 2.90 and 3.08 Å. This implies a tetrahedral or tetragonal distortion of the site, which cannot be suspected from the shape of our main edge, but which explains nicely the fine structure of the edge determined by Nakai *et al.* (1987) via their high-resolution operational set-up.

There is independent evidence supporting the distortion of the site. Even neglecting our own observation about the asymmetry of the Mg L-edge (too blurred by the experimental uncertainty problems to be reliable), we note that the absorption edges of several divalent metal ions crystallizing as monoxides isostructural with periclase (CaO, MnO, $Fe_{0.5}Mg_{0.5}O$, CoO, NiO: Knapp *et al.*, 1982; FeO: Petiau and Calas, 1982) all show fine strucutre. This has been interpreted either as due to presence of defects (vacancies), or more generally to irregularities around the octahedral site.

We interprete the major absorption peak at 562.0 eV as the first of EXAFS oscillations i.e. as the onset of the single scattering modes of the electrons ejected from the excited oxygen atom. We are aware that conventionally the EXAFS region should begin 50 eV above the edge, but this is only a conventional detail and other work is indeed in progress to fit this and the other observed EXAFS features into a broader model consistent with the rocksalt structure of periclase.

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