Ab initio calculations of the Ni *K*-edge XANES in Ni$_c$Mg$_{1-c}$O solid solutions

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An interpretation of the Ni *K*-edge X-ray absorption near edge structure (XANES) in pure NiO and Ni$_c$Mg$_{1-c}$O solid solutions is given based on three types of ab initio theoretical calculations: the full-multiple-scattering (FMS) approach, the finite difference method (FDM) and the full potential linear muffin-tin orbital (FP-LMTO) method within the LSDA+*U* approach. The first two methods differ in the cluster potential approximation: the spherically symmetric muffin-tin potential is used in the FMS approach, whereas a non-muffin-tin numerical potential makes the core of the FDM. We found that the FMS and FDM techniques allow rather accurate description of the experimental XANES signal especially above the absorption edge and produce close results, the FP-LMTO is more accurate close to the absorption edge.

X-ray absorption spectroscopy (XAS) became in the last ten years a routine structural tool, especially suitable to study the local environment around impurities or in multicomponent systems [1]. Traditionally, X-ray absorption spectrum is divided into two parts - X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The EXAFS is mainly due to the atomic structure around the absorber and can be rather well described within the multiple-scattering (MS) formalism [2]. At the same time, the MS series does not often converge in the XANES region, that requires the use of the full-multiple-scattering approach (FMS) or other theoretical techniques. Besides, the XANES part incorporates frequently contributions from transitions to empty localized electronic states and, thus, additionally provides an information on the local electronic structure of the absorber. Therefore, different advanced electronic structure calculation methods as, for example, ab initio linear muffin-tin orbital (LMTO) based methods [3] can be employed to perform more refined analysis of the XANES signals, at least close to the absorption edge.

In this work, we compare three theoretical methods, the FMS approach [4, 5], the finite difference method (FDM) [6] and the full potential linear muffin-tin orbital (FP-LMTO) method within the LSDA+*U* approach [7], on the example of NiO and Ni$_c$Mg$_{1-c}$O systems. The experimental details and qualitative interpretation of XANES were published by us previously [8, 9].

Pure nickel oxide NiO is a type-II antiferromagnetic charge-transfer insulator [10, 11]. Its dilution with non-magnetic magnesium ions [12, 13] results in a series of Ni$_c$Mg$_{1-c}$O solid solutions, whose magnetic properties vary from antiferromagnetic-like to diamagnetic-like behaviour [12, 13]. The crystalline structure of Ni$_c$Mg$_{1-c}$O solid solutions resembles closely that of NiO with the lattice parameter varying almost linearly with the composition [14]. The electronic structure of Ni$_c$Mg$_{1-c}$O solid solutions was stud-

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ied within ab initio unrestricted LCAO Hartree-Fock formalism in [15], and it was found that the density of Ni 3*d*-states in Ni$_c$Mg$_{1-c}$O are essentially independent of the composition [15].

Previous XAS studies [4, 5, 7, 16] were concerned with pure NiO, and the Ni *K*-edge XANES was analysed in [4, 5, 16] within the FMS approach. It was found [4] that the main features, observed in the experiment, are due to the scattering effects within about nine shells cluster of 6.6 Å radius, and the shells containing oxygen atoms produce more essential contribution than the ones composed of nickel atoms. In the most recent work [5], even better agreement was obtained using a self-consistent real-space Green's-function formalism. Besides the fine structure above the absorption edge, the pre-edge peak appears in NiO at about 8332 eV. It is associated with the quadrupolar $1s \rightarrow 3d$ transition, since Ni atoms occupy sites with inversion symmetry [17]. The same peak exists in all Ni$_c$Mg$_{1-c}$O solid solutions [8, 9].
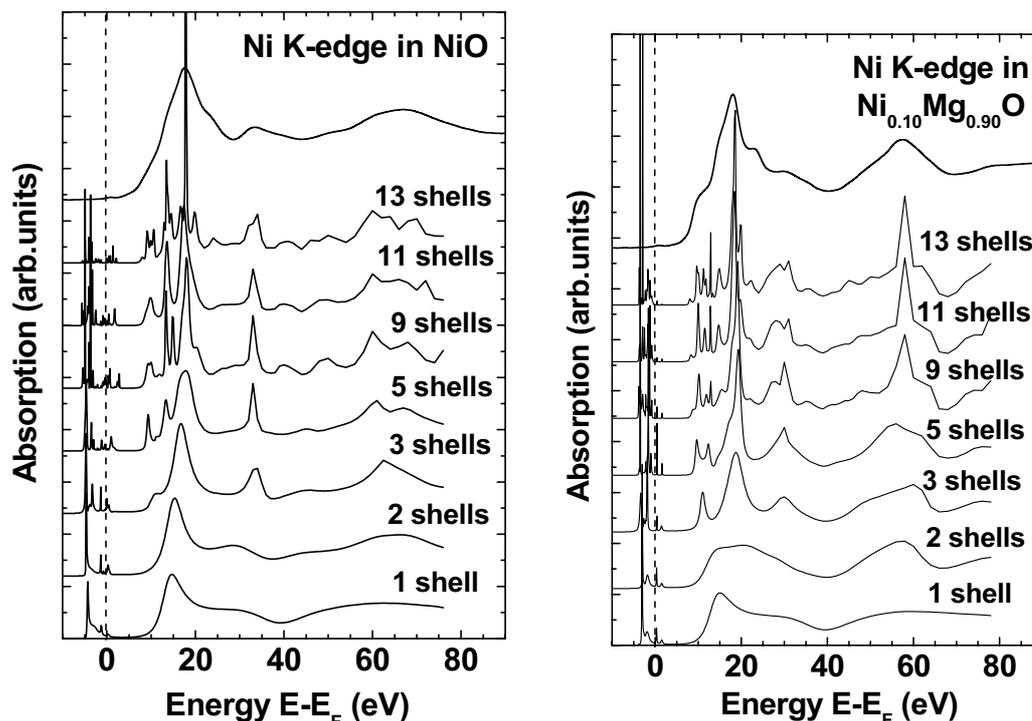

Fig. 1 Nickel *K*-edge XANES in NiO, calculated within the finite difference method, and in Ni$_{0.10}$Mg$_{0.90}$O solid solution, calculated within the FMS approach. Upper curves correspond to the experimental signals. Both calculations are done in the quadrupolar approximation. The number of coordination shells around absorbing nickel atom is given above the calculated XANES signals. The position of the Fermi's energy was shifted for theoretical signals to lower energies by 6 eV for NiO and by 8 eV for solid solution to best match the experimental data.

Further we will first discuss results of the calculations by the FDMNES code [6], performed in dipolar and quadrupolar approximations within the FMS and FDM approaches with the real Hedin-Lundqvist exchange potential. The two methods differ by the potential construction procedure: the FMS approach utilizes the spherical muffin-tin approximation, whereas a non-muffin-tin numerical potential, set on an equally spaced 3D-grid, is used in the FDM. It is believed that the non-muffin-tin corrections are crucial for correct description of the XANES signals especially for low symmetrical structures [6].

The calculations were performed for two extreme cases: pure NiO (a = 4.1778 Å) and infinitely diluted solid solution, in which all nickel atoms, except the central one, were exchanged with magnesium atoms. The clusters in both cases contained up to 251 atoms within 13 coordination shells. No broadening was applied to the calculated XANES signals. The representative results of the calculations are shown in Fig. 1.

The exchange of nickel atoms with magnesium ones results in more pronounced XANES features [8, 9], due to the differences in the scattering amplitudes and phase shifts of nickel and magnesium atoms. This effect is well reproduced by both theoretical approaches. In particular, good agreement for all features is obtained in the case of clusters, consisting of about 9 shells, as was found in [4]. The interpretation of the observed effects can be done using the results of the ab initio unrestricted Hartree-Fock calculations [15]. They indicate that the differences in the densities of states (DOS) as a function of composition are due to the changes in the intersite hybridization between nickel and oxygen orbitals [15]. The widths of nickel bands are determined by the number of superexchange interactions via oxygen atoms with smaller contributions from direct nickel-nickel interaction [15]. Therefore the widths increase slightly with an increase of the number of nickel neighbours, thus resulting in the broadening of the XANES features at high nickel concentrations.
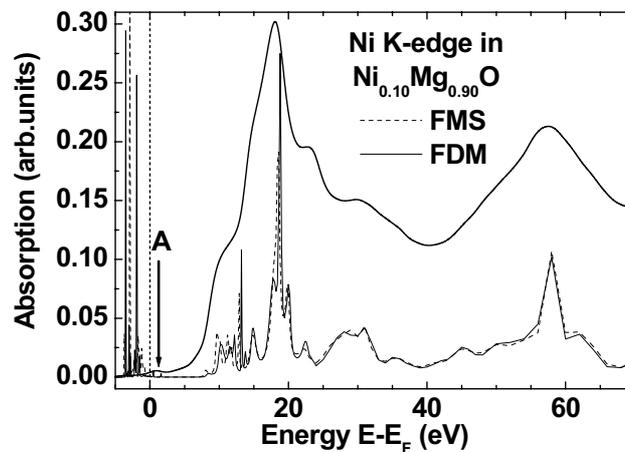

Fig. 2 Comparison of the Ni *K*-edge XANES in $Ni_{0.10}Mg_{0.90}O$ solid solution with the results of calculations for the cluster of 251 atoms by the finite difference method (FDM) and the full-multiple-scattering (FMS) approach. The pre-edge A position is indicated by arrow.
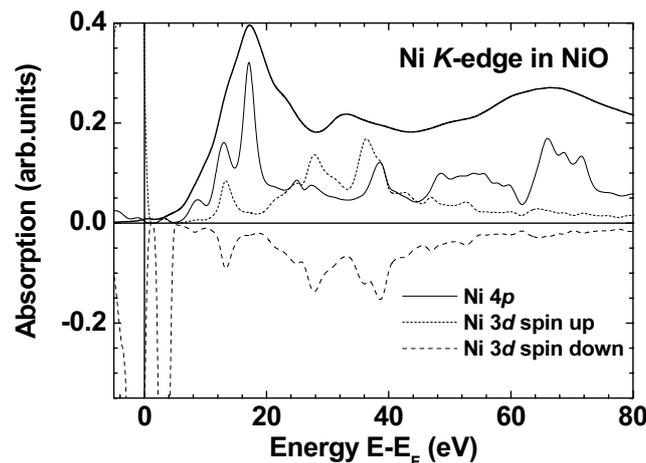

Fig. 3 Comparison of the Ni *K*-edge XANES in NiO with the Ni *p*- and *d*-projected unbroadened densities of states, calculated by the FP-LMTO method within the LSDA+*U* approach.

More detailed comparison of results, obtained by the FMS and FDM methods, is given in Fig. 2. Here the calculations were performed for the same 9 shells cluster. One can see that both methods produce

close results, especially far from the edge. However, some difference can be detected up to 15 eV above the Fermi level, where the peculiarities of the cluster potential are significant.

The pre-edge peak A, located just above the edge (Figs. 1 and 2), is present in both FMS and FDM calculations performed in the quadrupolar approximation, but is completely absent in the dipolar approximation. This result supports previously withdrawn conclusion [17] about the quadrupolar origin of the pre-edge.

Since Ni^{2+} is magnetic ion, more details about the pre-edge peak can be obtain by spin unrestricted theoretical calculations as the FP-LMTO method within the LSDA+U approach [7]. We used its realization in the LmtART code [18]. This method was successfully applied recently to the analysis of the oxygen K-edge in NiO [7], and its detailed description can be found in [18, 19]. The calculations were performed assuming the Hubbard parameter $U = 5$ eV and the exchange integral $J = 0.95$ eV, close to the values determined from the analysis of electron energy-loss spectra and total energy calculations for NiO in [2]. The radii of the muffin-tin (MT) spheres were equal to R(Ni) = 1.101 Å and R(O) = 0.984 Å. Note that no core-hole effect was included, opposite to the FMS and FDM calculations discussed above.

The obtained nickel p- and d-projected non-broadened DOS are compared with the Ni K-edge XANES signal in figure 3. Most features in the experimental XANES signal are well reproduced by the Ni p-DOS, suggesting that the dipolar $1s \rightarrow np$ transitions dominate above the edge. Moreover, good agreement in the energy positions of the calculated Ni p-DOS maxima and experimental XANES features suggest small core-hole effect for this case. The pre-edge peak can be attributed to the quadrupolar transition $1s \rightarrow 3d(e_g\downarrow)$. Here, the small size of the quadrupolar matrix element, compared to the dipolar one, is compensated by the large amount of the $3d(e_g\downarrow)$ DOS (Fig. 3).

As a conclusion, we have demonstrated that all three theoretical methods - FMS, FDM and FP-LMTO, can be successfully used in the analyses of the Ni K-edge XANES in NiO and Ni$_c$Mg$_{1-c}$O solid solutions. The first two methods give better results above the edge, whereas the last method is more accurate close to the Fermi's level. Comparison of the FMS and FDM results suggests that the non-muffin-tin corrections to the potential are probably not so crucial in the case of studied systems. Also the core-hole effect seems to be small enough.

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