Near-edge structure in electron-energy-loss spectra of MgO

Th. Lindner, H. Sauer, W. Engel, and K. Kambe
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, Federal Republic of Germany
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Electron-energy-loss spectra of all core-level absorption edges of MgO microcrystals were recorded in the transmission mode using 60-keV electrons. The low-noise signal attained at a resolution of 0.5 eV reveals details of fine structure in the near-edge region. The spectra obtained were analyzed by the application of multiple-scattering theory to the cluster model. For comparison, calculations of the projected density of states derived from Korringa-Kohn-Rostoker band structure are presented. An overall agreement between measurement and theory is achieved. Remaining deviations in details are discussed.

Studies of the x-ray-absorption near-edge structure, both theoretical and experimental, have been of considerable interest.[1] The same type of experiment, namely, the excitation of inner-shell electrons, can be performed in electron-energy-loss spectroscopy (EELS) with fast electrons, yielding similar structure, called electron-energy-loss near-edge structure (EELNES). If the signal in EELS is collected only from small scattering angles, optical (dipole-allowed) transitions dominate the cross section. The theoretical models for EELNES are therefore taken from the x-ray-absorption analog. In this study we compare experimental data with the results of model calculations to clarify the underlying physical mechanisms.

The instrument used for the measurements was constructed especially for EELS with fast electrons. It consisted of a scanning transmission electron microscope with a field emission gun and an electron spectrograph. The spectrograph permitted simultaneous recording of a whole spectrum in a chosen energy range. Data acquisition was performed through an optical multichannel analyzer which provided the spectra in digitized form for further processing. The spectra presented were recorded with the energy of the primary beam fixed at 60 keV. The half-angle of acceptance was kept below 10^{-2} rad; the energy resolution was 0.5 eV. The absolute values of the energy loss were determined to an accuracy of ± 0.2 eV. The recording time for one spectrum was 5 min. The samples used were single-crystalline smoke particles of MgO, prepared by burning a magnesium ribbon in air and collecting the smoke onto a holey carbon film. In order to reduce background due to multiple losses, crystal platelets which protruded over the holes were used for measurements. Sample thickness was estimated to be 500 Å. The area illuminated for recording spectra was typically $0.2 \times 0.2\ \mu m^2$ with a current of the order of 10^{-9} A.

In our theoretical investigation, we used two approaches: short-range-order (cluster model) and long-range-order (band-structure) theory. The cluster calculation was performed using the computer code of Durham, Pendry, and Hodges.[2] In MgO the absorbing atom is in a cubic environment and an average over the directions of momentum transfer[3] is justified. This also permits calculation of EELNES above the Mg $L_{2/3}$ edge, where the contributions of the different angular momentum components of the final states are assembled as a weighted sum according to Eqs. (23) and (16) of Ref. 3. The projected densities of states have been derived from a Korringa-Kohn-Rostoker band-structure calculation by using a relatively rough subdivision of the Brillouin zone (corresponding to 2048 or 6912 simple-cubic mesh points), remedied by a relatively large lifetime broadening corresponding to the imaginary part of energy, -0.5 eV. In both theories the same potentials (characterized by the scattering phase shifts) were used. They were constructed as spherically averaged superposition potentials (with $\alpha = \frac{2}{3}$ the multiplication factor for the exchange potential) from Clementi free-atom Hartree-Fock wave functions[4] and employed successfully to explain low-energy electron diffraction experiments.[5] For comparison with experiments, the core-hole effect of the absorbing atom was taken into account only for K edges in the cluster model. This was done by the so-called $Z+1$ approximation; i.e., the central atom with a K hole was replaced by the atom next in the Periodic Table. For Mg ($Z=12$) we used the muffin-tin potential data ($\alpha=\frac{2}{3}$) of Snow[6] for metallic Al ($Z=13$). For O ($Z=8$) we took the free-atom data for F ($Z=9$) from Clementi[4] (interpolated by Cox and Bonham[7]) and derived the potential data with $\alpha=\frac{2}{3}$. We remark that the form of the muffin-tin potentials used does not account for the Coulombic tail of the core-hole potential.

The experimental curve in Fig. 1 showing the EELNES above the Mg K edge was processed in the following way: The background absorption curve preceding the edge was fitted to an inverse power law. This was extrapolated beyond the edge and subtracted. The remaining contribution of the inner-shell excitation was deconvoluted with respect to the low-loss spectrum (mainly interband transitions and plasmon loss) using a modified Fourier-division method.[8] We emphasize that owing to the already favorable sample thickness this procedure is only a small correction to the measured spectra. In effect it only changes the relative amplitudes of the peaks. It does not change either the energy positions or the shape of the observed peaks. In Fig. 1 the label "shell" denotes the set of

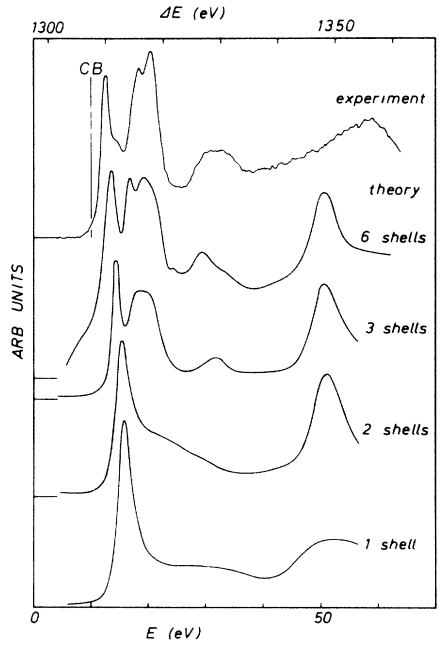

FIG. 1. Mg K edge. The experimental curve is background stripped and deconvoluted. The lower four curves give the transition rate calculated in the cluster model using the $Z+1$ approximation. Phase shifts up to $l=3$ are used. Damping is -1.0 eV for the six-shell cluster, otherwise zero. For the alignment of the energy scales according to Eq. (1) and the determination of the conduction-band edge (CB) see text.

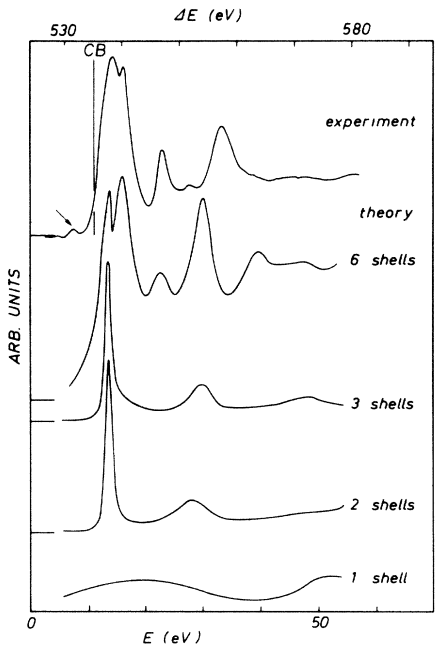

FIG. 2. O K edge. All notations and parameters are the same as in Fig. 1.

atoms at the same radial distance from the absorbing atom. Damping, which is here an imaginary part added to the energy of the excited electron, was included only for the six-shell cluster calculation. The value chosen for obtaining good agreement with experiment was -1.0 eV. The alignment between the energy scales for experiment and theory is performed by the relation

$$E=\Delta E-(E_{\mathrm{MT}}-E_c)\,, \tag{1}$$

where ΔE is the energy loss of the primary electron, E_{MT} is the constant level of the muffin-tin potential which is the zero of energy E for all the calculations, and E_c is the binding energy of the core level. The quantity $E_{\mathrm{MT}}-E_c$ is adjusted so that the positions of the first peaks of the measured and calculated curves match. Figure 2 contains the set of corresponding curves for the O K edge. In Fig. 3 the measured Mg L_1 and $L_{2/3}$ EELNES are plotted in the same manner; the calculation is shown only for the six-shell cluster.

The model calculations in Figs. 1 and 2 show that the two constituents of the compound contribute differently to the transition rate. In MgO that has the NaCl structure, subsequent shells are made up of the two atomic species alternatingly. In Fig. 1, for Mg the central atom, the first shell, consisting of six O atoms, already gives rise to a relatively sharp peak. Around the O center, however, a second shell—which then consists of 12 O atoms—is necessary to produce the same effect. This demonstrates the influence of the relatively strong backscattering of the O^{2-} ion. This is in accordance with recent calculations for NiO.[9] The result can be understood as a caging effect of the O shell on the excited electron: The backscattering creates a relatively sharp quasibound scattering resonance around the absorber atom. The inclusion of more shells in the calculation introduces more peaks in the transition rate. This indicates that more resonances are introduced. The detailed identification of these resonances has not yet been achieved. It is clear that the structure finally goes over to the projected local density of states of the infinite lattice.

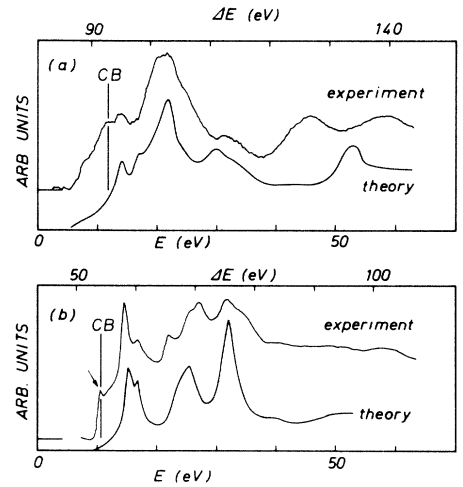

FIG. 3. (a) Mg L_1 edge. The theoretical curve is calculated with a six-shell cluster using the unexcited (Z atom) central atom potential. Parameter values are the same as in Fig. 1. (b) Mg $L_{2/3}$ edge. Same set of curves as in (a). Phase shifts up to $l=2$ are used. Damping is -0.5 eV.

The influence of the core-hole potential can be studied by comparing the Mg K with the Mg L_1 edge. In both cases the final states have p symmetry. However, the argument for the $Z+1$ approximation to be used[10] does not apply for the L edges. Both theory and experiment show significant changes in the relative intensities of the peaks and only slight changes in the peak positions [Fig. 3(a) compared to Fig. 1].

Aside from the possible core-hole effects, there remain general discrepancies between calculated and measured peak positions. It is possible that they are due to the neglect of the energy dependence of the potentials. The importance of considering energy-dependent exchange and correlation effects for the correct treatment of extended x-ray-absorption fine structure (EXAFS) has long been recognized. It has also been emphasized that in the near-edge region the situation is more difficult than in the EXAFS region.[10] The importance of considering the correlation in band-structure calculations has also been demonstrated explicitly.[11] It is interesting to note that similar differences have also been observed in bremsstrahlung-isochromat spectroscopy,[12] where no core hole is created.

We emphasize the observation of two features that do not appear in the calculated spectra at all [marked with arrows in Figs. 2 and 3(b)]. We tentatively interpret them to be core excitons, as they are expected to contribute significantly in the vicinity of absorption edges.[13] This interpretation is supported by the fact that the two peaks seem to lie below the conduction-band edge, marked CB in Figs. 1–3. We have utilized the prescription of Pantelides[13] to determine the conduction-band edge by using the energy difference between the core level and the top of the valence band as determined from x-ray-emission data,[14] together with an optical band gap of 7.77 eV.[15] We also determined the band gap from the rise of the absorption in the low-loss spectrum to be 7.7 ± 0.1 eV. We have found, thus far, that the cluster calculations are able to reproduce all essential features of the measured spectra.

In order to check the reliability of the cluster model with respect to its limited size, we compared the results with those of the band-structure calculation. Examples of the p-projected densities of final states are shown for the Mg site in Fig. 4(a) and the O site in Fig. 4(b), with the corresponding cluster calculations below each curve.

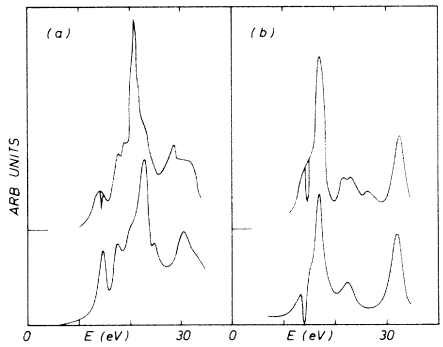

FIG. 4. Upper curves give the p-projected densities of states as derived from the band-structure calculation. Lower curves give the transition rates as calculated in the cluster model. In (a) the origin is at the Mg site, in (b) at the O site. Both approaches use phase shifts up to $l=2$. Damping is -0.5. eV.

From the good agreement we conclude that a cluster of six shells (80 atoms) already describes bulk properties; i.e., the cluster model converges sufficiently to reproduce the local densities of states. Note that the cluster calculations in Figs. 4(a) and 3(a) are performed using the same potential, the essential difference lying only in the amount of damping.

We have shown that the observed near-edge structures are in agreement with the symmetry-projected local densities of states. In contrast to the case of L absorption, the presence of the core hole cannot be neglected in the case of K edges. Our results indicate that a quantitative comparison of experiment and the presented theory is possible. The remaining deviations, particularly the possible presence of core excitons, indicate the need for more refined methods in calculating excited states.

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