dd excitations of NiO studied with L_3 RIXS: experiment and crystal field simulations

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NiO

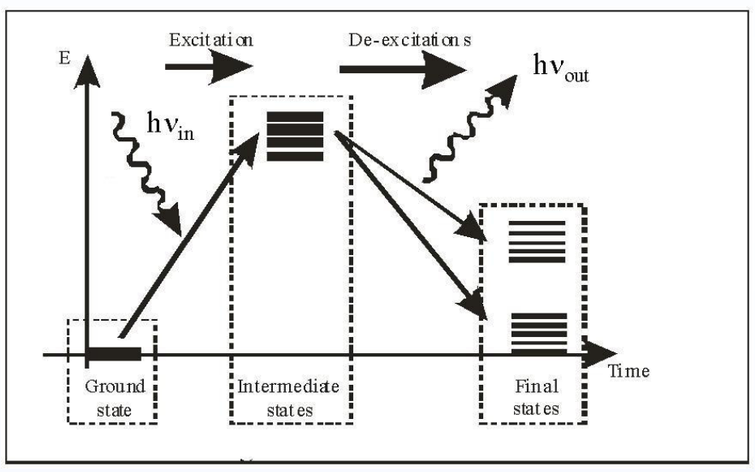
The interest in transition metal compounds is due to their properties like high-T_c superconductivity and giant magnetoresistance.

NiO has a rocksalt cubic structure, each Ni^{2+} ion is octahedrally surrounded by six O^{2-} ions. NiO is antiferromagneticbelow the Néel temperature (523 K). Ni^{2+} fundamental configuration is $2p^63d^8$, the issue of the measurements and the simulations is to study the excited levels near the ground state.

RIXS technique

In RIXS (Resonant Inelastic X-Ray Scattering) technique a core electron is resonantly excited to the threshold region by an incident photon. The created hole is then neutralized by a valence electron, with the emission of an x-ray photon. The transferred energy $h\nu_{out}$-$h\nu_{in}$ spectra show peaks at $h\nu_{out}$-$h\nu_{in}$<0 that reveal the presence of the excited levels near the ground state, that has $h\nu_{out}$-$h\nu_{in}$=0.

In our measurements a 2p photon is excited to 3d states, the 2p hole is then filled by one 3d electron. This technique is bulk sensitive.



dd excitations

In contrast to free atoms, where the d-states are degenerate, the d-states of transitions metal ions in the oxides are energetically split because of the crystal field, provided by the surrounding oxygen ions. Direct electric dipole transitions between 3d states (*dd* excitations) are forbidden by selection rules. With RIXS technique there are two dipole transitions involved, so *dd* excitations are observable.

The 3d electrons in transition metal oxides , like in NiO, have local nature, so *dd* excitations have local character and can be studied with the crystal field model.

The simulations

Simulations are based on the Cowan's atomic model, with a correction for considering the crystal field. We considered the process $2p^63d^8 \rightarrow 2p^53d^9 \rightarrow 2p^63d^8$. The calculations were made in C_{4h} simmetry, with 110° scattering angle. At the experimental temperature, NiO is antiferromagnetic, its atoms have local magnetic structure but the total magnetization is null. To simulate this situation we have done the arithmetic average of three cases: atomic moment perpendicular to the scattering plane, or in the scattering plane both along the emission direction or at 20° from the incidence radiation.

The experiment

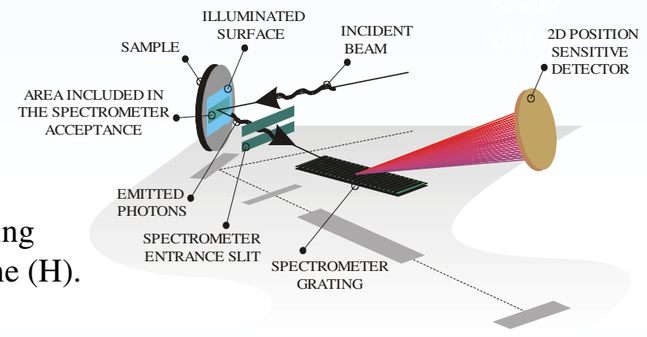
The experiment was performed on ID08 at the European Synchrotron Radiation Facility in Grenoble, with the high resolution spectrometer AXES and the dedicated soft x-ray monochromator PoLIFEMo.

The incident radiation had energy near L_3 edge of Ni (853 eV). The sample was single crystal, at room temperature.The angle between incident and emitted beam was 70°, with normal emission to minimize self-absorption effects.

The incident beam polarization was linear, perpendicular to the scattering plane (V) or lying in the scattering plane (H).

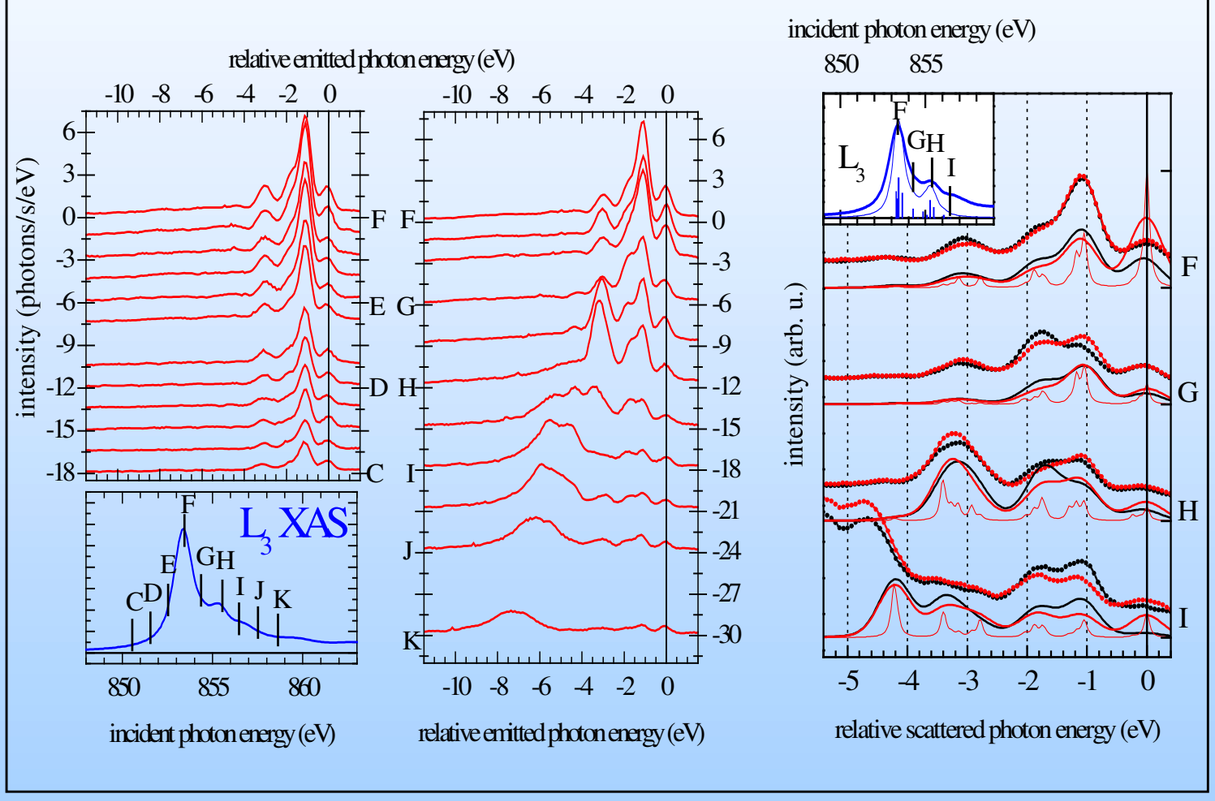
The energy resolution was 650 meV.

Spectrometer AXES installed at ID08 of the ESRF[2]



Results

For the simulation the best agreement between calculations and measurements was obtained for these values: 10 Dq=1.05 eV, exchange force =120 meV, Slater integral reduction 70%, intermediate state life time broadening = 300 meV, final state lifetime =100 meV. The calculated spectra were then convoluted with a Gaussian 600 meV FWHM to simulate the experimental resolution.



Conclusions

With RIXS technique we observed *dd* excitations of NiO. The good agreement between calculations and measurements confirms that *dd* excitations can be interpretated with a crystal field model. These transitions have local character. By comparing simulated spectra with the measurements we could optimize the values of calculations parameters.