# Crystal field excitations in MnO measured with RIXS (Resonant Inelastic X-Ray Scattering)

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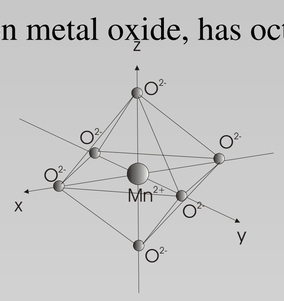
## Motivation

Electronic excitations due to the crystal field are traditionally measured with optical spectroscopy or Electron Energy Loss Spectroscopy. High resolution RIXS at the $L_3$ edge of 3d transition metals can be an important alternative to tried techniques. MnO is a paradigmatic compound that can be used to evaluate the power of RIXS.

## MnO

MnO, example of transition metal oxide, has octahedral structure.

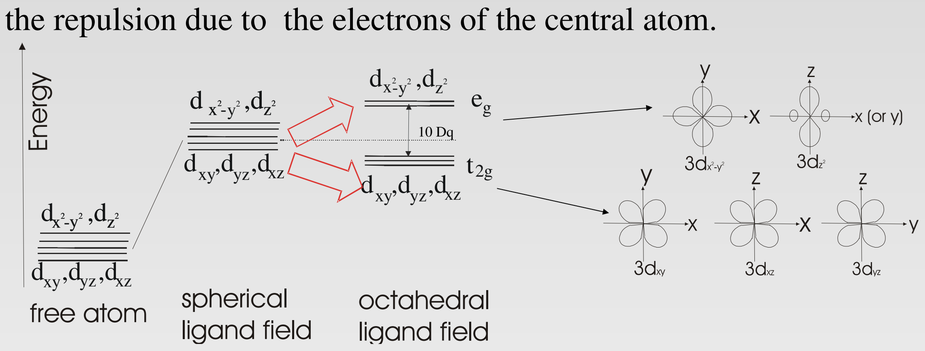



It's antiferromagnetic below the Néel temperature (122 K).

The fundamental configuration for $Mn^{2+}$ is $2p^6 3d^5$.

## *dd* excitations

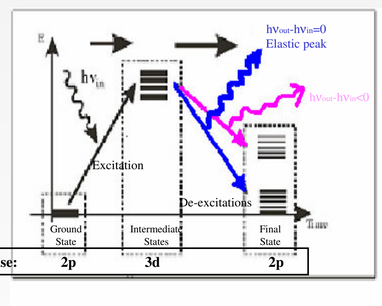
MnO has 3d electrons over the completed shell.
The crystal field of the ligands causes an increase of energy of these states proportional to the repulsion due to the electrons of the central atom.

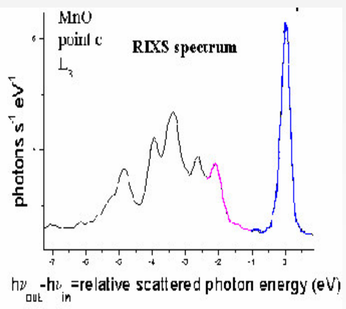


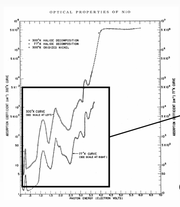

The five 3d states, degenerate in a free atom, are split.
The direct transition from a 3d state to another is called *dd* excitation. *dd* excitations have local character.

## RIXS technique

RIXS (Resonant Inelastic X-Ray Scattering) technique consists in exciting resonantly a core electron 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. This technique is bulk sensitive. Direct electric dipole transitions between 3d states (*dd* excitations) are forbidden by selection rules. With the RIXS technique there are two dipole transitions involved, so *dd* excitations are observable.



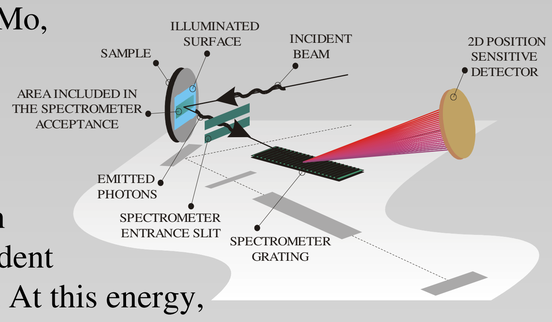



*dd* excitations can be measured also with optical absorption but with low intensity: they are forbidden by selection rules. It is also difficult to interpret the peak intensities.

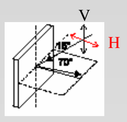
Optical absorption spectrum of NiO from R. Newman and R. M. Chrenko, Phys. Rev. 114, 1507 (1959)

## The experiment

The spectra were measured with the high resolution spectrometer AXES and the dedicated soft x-ray monochromator PoLIFEMo, made in Milano, property of INFM, installed on ID08 at the European Synchrotron Radiation Facility in Grenoble.




Its combined resolving power is high: more than 1500 for all the heavy 3d transition metals. RIXS spectra were taken with an incident photon energy near $L_3$ edge (640 eV for Mn). At this energy, the full width at half maximum of the elastic peak is smaller than 320 meV.
The sample was a single crystal,measured at room temperature.
There were 70° between incident and emitted beam, the emission was normal to minimize self-absorption effects.
The polarization could be normal (Vertical) or parallel (Horizontal) to the scattering plane.

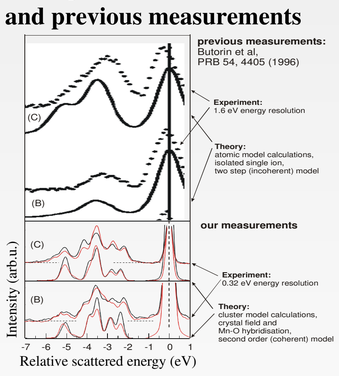


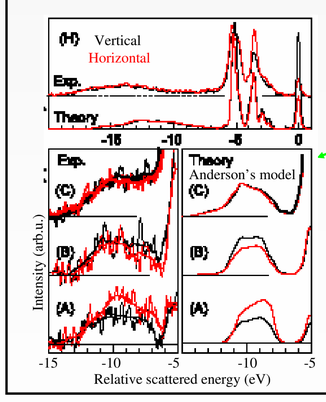

## Results

We have measured low energy excitations for MnO[1].
The measurements present many features.
With the single impurity Anderson model, which considers also the interaction between the Mn ion and the continuum of the crystal, we reproduced *dd*[1,2,3] and charge transfer[1,2,3] excitations (in which an electron is transferred from the ligand $O^{2-}$ to the $Mn^{2+}$ ion).
With a code based on the Cowan's atomic model[2] corrected to consider the crystal field we can reproduce peak positions, intensity and polarization of the structures due to *dd* excitations.

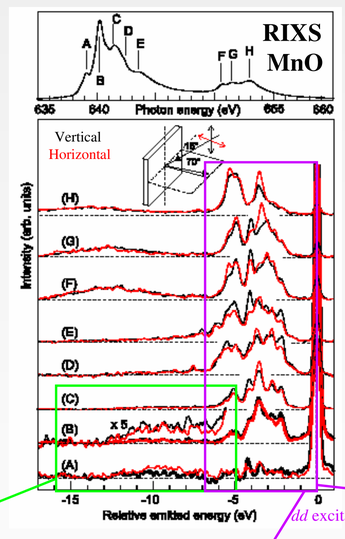
[1] G.Ghiringhelli, M.Matsubara, C.Dallera, F.Fracassi, A.Tagliaferri, N.B.Brookes, A.Kotani, L.Braicovich, Phys. Rev. B **73**, 035111 (2006)
[2] R. D. Cowan, 'The theory of atomic structure and spectra' (University of California Press, Berkeley, 1981)
[3] R. Butorin et al., Phys Rev. B **54**, 4405 (1996)

**Comparison between our and previous measurements**

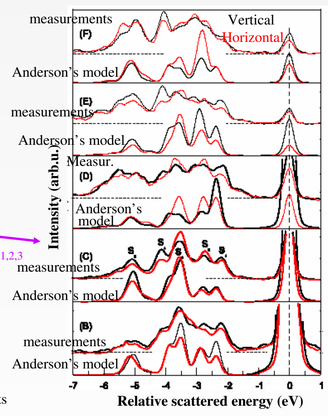



**Our measurements[1]**

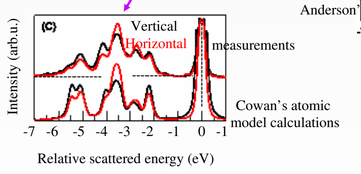



| Calculations: | 10 Dq | Slater reduct. |
|---|---|---|
| Anderson's model | 0.5 eV | 80% |
| Cowan's model | 1.00 eV | 75% |




*dd* excitations [1,2,3]

Charge transfer excitations [1,2,3]




## Conclusions

**With RIXS technique we observed *dd* excitations. RIXS results can be directly compared to optical spectroscopy results. With RIXS, *dd* excitations are not forbidden and it's easier to calculate the spectral intensity because the process can be explained by a simpler model.**