# Spin-resolved NEXAFS from resonant X-ray scattering (RXS)

**G. Dräger[a]*, Th. Kirchner[a], S. Bocharov[a], and C.-C. Kao[b]**

[a]*Fachbereich Physik, Martin-Luther-Universitaet Halle-Wittenberg, 06108 Halle, Germany,*
[b]*NSLS, Brookhaven National Laboratory, Upton, NewYork 11973 USA. E-mail: draeger@physik.uni-halle.de*

Resonantly excited metal K core line spectra of NiO, MnO, CoO and other compounds have been investigated at the beamlines X21 (NSLS/BNL), BW1 and W1.1 (HASYLAB/DESY). From analysis of spectral data we have drawn the following conclusions: -spin conservation is valid in the scattering process, for excitations below the absorption threshold as well as above it, -the absorption thresholds are different for spin-up and spin-down components of resonantly scattered spectra, -quadrupole transitions are very important or even crucial in the excitation process. Provided that these conclusions are true, a novel technique for quantitative resolution of NEXAFS spectra into spin-up and spin-down components has been developed. Since the method employs spin conservation and local spin references, it needs no circularly polarized radiation and no sample magnetization for taking both the RXS and NEXAFS spectra. Hence antiferromagnetic and paramagnetic materials can be investigated as well. Utilizing linear dichroism by angular-dependent measurements on single-crystal samples additional resolution of NEXAFS spectra is possible with respect to the orbital symmetry. Application of the method to paramagnetic MnO, for the first time, provides new and unambiguous experimental results confirming modern (LSDA+U) calculations: The metal K pre-edge XAS of MnO has predominantly 3d(t2g and eg) spin-down character. On the other hand, the delocalized p-like states, arising from the p-d band effect hybridization have spin-up character.

**Keywords: spin-resolved NEXAFS, resonant X-ray scattering, 3d-transition metal oxides.**

## 1. Introduction

X-ray absorption spectroscopy is a powerful tool for probing the electronic structure of solid state materials. Utilizing the effect of magnetic circular dichroism (MCD) spin-polarized spectral densities of magnetized ferro- and ferrimagnetic materials can be investigated by using the well established techniques working with circularly polarized radiation. For an antiferromagnetic sample, however, the MCD effect is canceled, because the magnetic sites are always 50% spin up and 50% spin down. Here the local-spin-selective X-ray absorption spectroscopy (Hämäläinen et al., 1992) can help. By measuring fluorescence-yield at selected energies of appropriate core emission lines the excitation spectra so obtained are referenced to defined magnetic sites and reflect their spin-up and spin-down parts. This technique works only qualitatively and, therefore, the results will be used for qualitative comparison with model calculations (Wang et al., 1997).

We report an experimental method to investigate the spin-projected **N**ear-**E**dge **X**-ray **A**bsorption **F**ine **S**tructure (NEXAFS) of transition metal compounds by resolving their transmission **X**-ray **A**bsorption **S**pectra (XAS) by means of core line **R**esonant **X**-ray **S**cattering (RXS) spectra. Since the method employs spin conservation and local spin references, it needs no circularly polarized radiation and no sample magnetization. Hence, the spectra of antiferromagnetic and paramagnetic materials can be resolved as well. Moreover, by angular-dependent measurements of spectral data on single-crystal samples the resolution of conduction-band states with respect to their orbital symmetry is also possible.

## 2. Experimental

Resonantly excited metal K and L core line spectra of NiO, MnO, CuO and other compounds have been investigated at the beamline X21 at NSLS/BNL and at the beamlines BW1 and W1.1 at HASYLAB/DESY. The experimental arrangements are shown in Figs. 1 and 2.

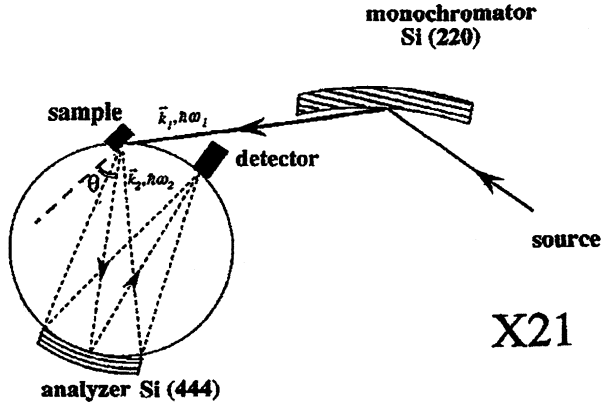


**Figure 1**
Sketch of the Johann spectrometer with spherically bent crystal used for RXS measurements at the beamline X21 (NSLS/BNL).

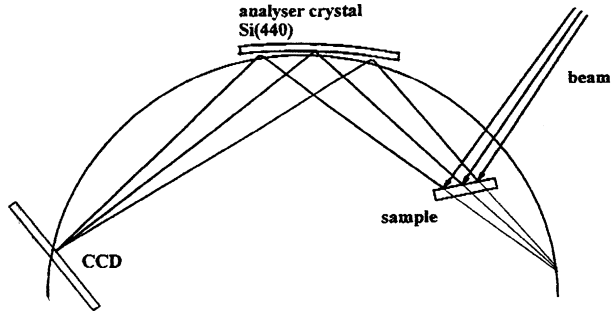


**Figure 2**
Sketch of the Johann spectrometer with cylindrically bent crystal and X-ray CCD detector used for RXS measurements at the beamlines BW1 and W1.1 (HASYLAB/DESY).

NEXAFS spectra has been measured in the transmission mode at the beamline A1 (HASYLAB/DESY). NEXAFS and core line RXS spectra of single-crystal samples have been recorded for selected orientations of the crystal axes of the sample with respect to the polarization $\vec{e}$ and the wave vector $\vec{k}$ of the exciting radiation. In these experiments we found a strong orientation dependence in the NEXAFS and RXS spectra as well. As an example we show in Fig. 3 the resonantly scattered Cu $K\alpha_{1,2}$ emission for two orientations of a single-crystal CuO sample and for several excitation energies. The dedicated energies belonging to the two orientations are marked in the Cu K-NEXAFS spectra which are measured in a transmission geometry.

  

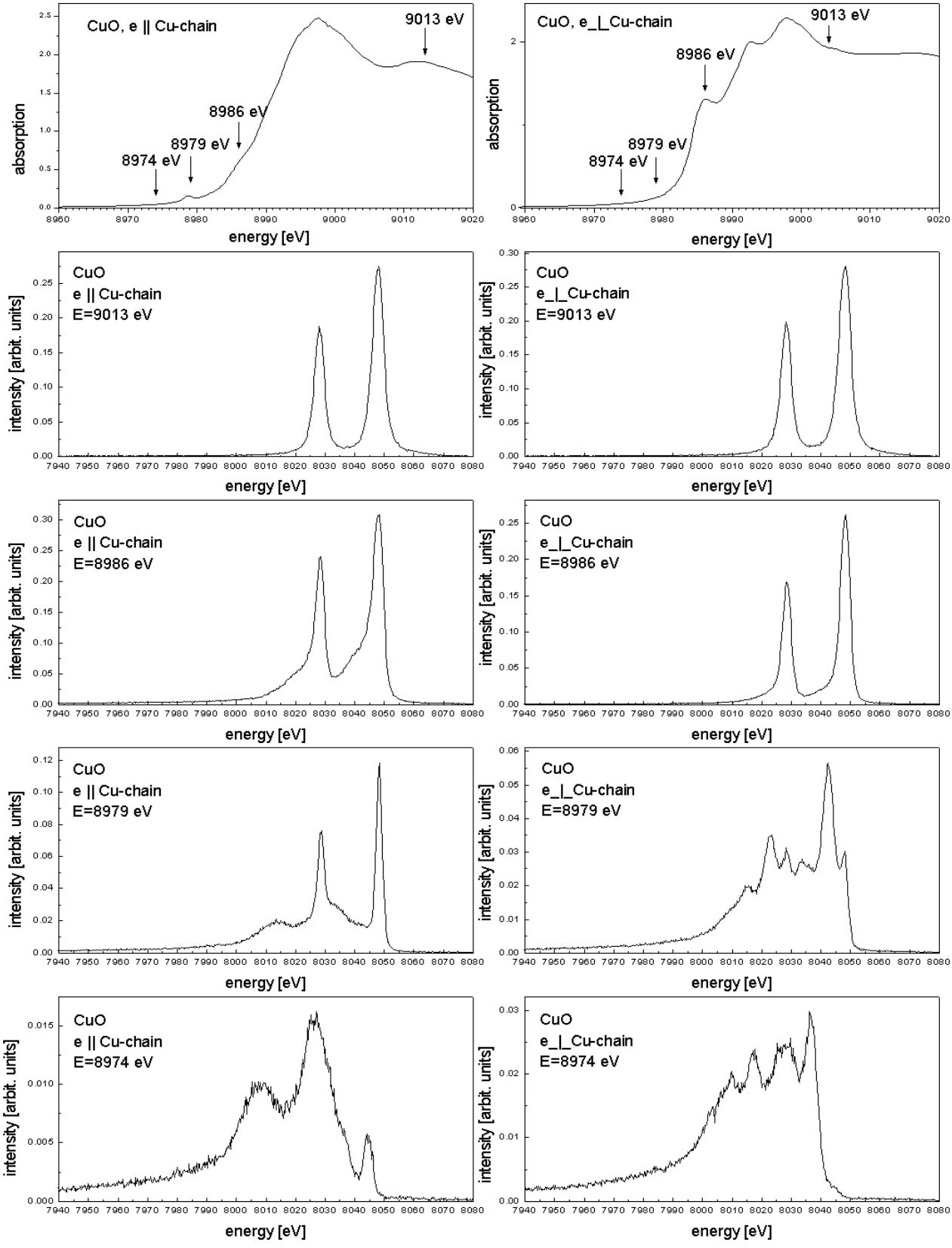


**Figure 3**
The resonantly excited Cu Kα emission spectra of a single-crystal CuO sample for two orthogonal orientations with respect to the polarization vector of the incident beam (left and right column) and for four different excitation energies (lower four rows). The dedicated excitation energies belonging to the two orientations are marked in the Cu K-NEXAFS (upper row), which was measured in transmission geometry.

Both spectra show a strong orientation dependence, the Cu K-NEXAFS over the whole region as shown, the Cu $K\alpha_{1,2}$ RXS for excitation energies at least in the region of the pre-edge and main edge absorption.

### 3. The method of spin-resolved NEXAFS by core line RXS

From the analysis of spectral data (resonantly scattered $K\alpha_{1,2}$ and $K\beta_{1,3}\beta'$ core line spectra of NiO, MnO, CuO a.o.m.) we have drawn the following conclusions:
-spin conservation is valid in the scattering process, for excitation below the absorption threshold as well as above it,
-the absorption threshold are different for spin-up and spin-down components of resonantly scattered spectra,
-quadrupole transitions are very important or even crucial in the excitation process.

Provided that these conclusions are right, a novel technique for quantitative resolution of NEXAFS spectra into spin-up and spin-down components has been developed. This will be demonstrated for the example of spin-resolving the Mn K-NEXAFS of MnO by evaluation of its resonantly scattered Mn $K\beta_{1,3}\beta'$ core lines.

Assuming only spin-conserving transitions in the resonant X-ray scattering process the complementary spin parts x for the up spin $\uparrow$ and (1-x) for the down spin $\downarrow$ in the K absorption spectrum can be determined from the intensity ratio of appropriate spin-polarized core emission components. In the case of analysing the resonant Mn $K\beta_{1,3}\beta'$ emission of MnO we suppose the ratio x/(1-x) of spin-up and spin-down states to be the same for the excited conduction-band states (and the produced Mn 1s holes in the intermediate states), as for the resonantly scattered spin-resolved Mn $K\beta_{1,3}\beta'$ photons (and the resulting Mn 3p holes in the final state). Following this, we have to resolve the resonantly scattered Mn $K\beta_{1,3}\beta'$ emission into spin-polarized components and to determine the x/(1-x) ratio.

The resonantly scattered core lines $K\beta_{1,3}\beta'$ has been resolved into their spin polarized components by using special fitting methods.

### 4. The spin-resolved Mn K-NEXAFS of MnO

The spin-resolved Mn K-NEXAFS of a single-crystal MnO sample are shown in Figs. 4 and 5.

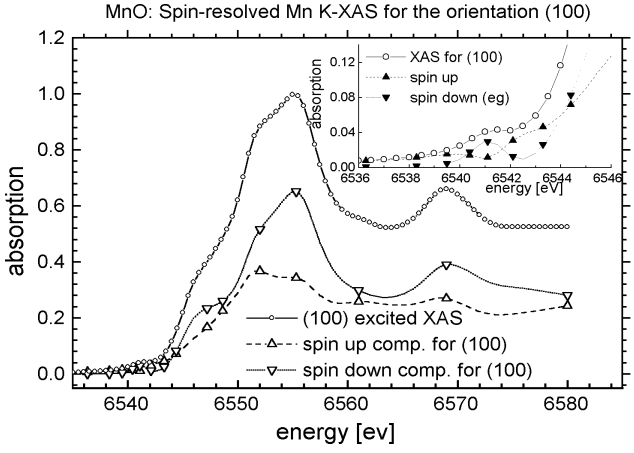


**Figure 4**
For the (100) orientation the $1s \rightarrow 3d(e_g)$ transition is quadrupole allowed. In the orbital- and spin-resolved NEXAFS only the empty $3d(e_g)$ spin-down states can be seen at about 6541.1 eV.

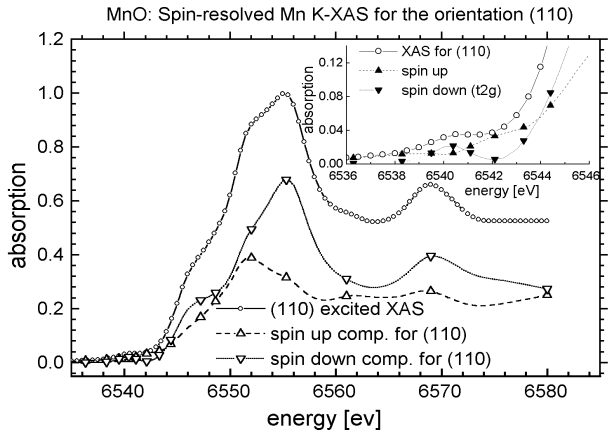


**Figure 5**
For the (110) orientation the $1s \rightarrow 3d(t_{2g})$ transition is quadrupole allowed. In the orbital- and spin-resolved NEXAFS only the empty $3d(t_{2g})$ spin-down states can be seen at about 6540.3 eV.

The resolution has been performed for two different orientations (100) and (110) of the sample with respect to the polarization $\vec{e}$ and the wave vector $\vec{k}$ of the excitation. For orientation (100) only the 1s→3d(eg) quadrupole transition is allowed, for the orientation (110) the 1s→3d(t2g) transition only.

The detailed analysis of the Mn K-NEXAFS of MnO by means of its orientation dependence and of the resonantly scattered Mn $K\beta_{1,3}\beta'$ spectra provides two well resolved pre-edge absorption peaks split by about 0.8 eV. These could be identified as $3d(e_g\downarrow)$ and $3d(t_{2g}\downarrow)$ states, both in agreement with the theory (Terakura et al., 1984; Hugel & Kamal, 1996; Massida et al., 1997). On the other hand, the delocalized p-like states, arising from the p-d band effect hybridization have spin-up character.

This research was supported by Deutsche Forschungsgemeinschaft DFG, by National Synchrotron Light Source NSLS and by Hamburger Synchrotronstrahlungslabor HASYLAB.

### References

Hämäläinen, K., Kao, C.C., Hastings, J.B., Siddons, D.P., Berman, L.E., Stojanoff, V. & Cramer, S.P. (1992). *Phys. Rev.* B46, 14274-14277.
Hugel, J. & Kamal, M. (1996). *Sol. Stat. Comm.* 100(7), 457-461.
Massida, S., Continenza, A., Posternak, M. & Baldareschi, A. (1997). *Phys. Rev.* B55(20), 13494-13502.
Terakura, K., Oguchi, T., Williams, A.R. & Kübler, J. (1984). *Phys. Rev.* B30(8), 4734-4747.
Wang, X., de Groot, F.M.F. & Cramer, S.P. (1997). *Phys. Rev.* B56(8), 4553-4564.

 Received 31 July 2000 • Accepted 13 November 2000 