Linear dichroism in 3d transition metal NEXAFS of correlated materials

Guenter Draeger*, **Sergey Bocharov, Thomas Kirchner, and Nadejda Kirchner**

Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, 06108 Halle, Germany.
E-mail: draeger@physik.uni-halle.de

Investigations of 3d transition metal (TM) compounds by means of linear dichroism in TM K-NEXAFS will be reported. At this, the decomposition of the angular-dependent NEXAFS into orbital projected components are important problems. A survey is given on methods how to extract information on the geometrical, electronic and magnetic structure from linearly polarized NEXAFS and EXAFS spectra. New results on CuO and CuPc (Copper Phthalocyanine) are reported. A reference is given to the novel method for spin-resolving of NEXAFS by analysis of resonantly scattered X-ray core lines.

Keywords: NEXAFS, partial density of states, 3d transition metal compounds, spin-resolved spectral components.

1. Introduction

The 3d metal oxides and other compounds acquire a particular interest as the subjects of electron-electron correlation study. Regarding their polarized K-NEXAFS we try to refine the experimental data in such a way, that they can be directly compared with the site-projected angular momentum resolved densities of empty states at the metal site.

2. Experimental

Linear dichroism in Near-Edge X-ray Absorption Fine Structure (NEXAFS) can be investigated in a transmission geometry as shown in Fig. 1. Linearly polarized synchrotron radiation transmits a single-crystal absorption sample which can be oriented with respect to the polarisation vector $\vec{e}$ and the wave vector $\vec{k}$ of radiation by three perpendicular rotations φ, θ, ψ. From the transmitted intensity the energy- and orientation-dependent X-ray absorption coefficient $\mu(\hbar\omega, \vec{e}, \vec{k})$ can be evaluated.

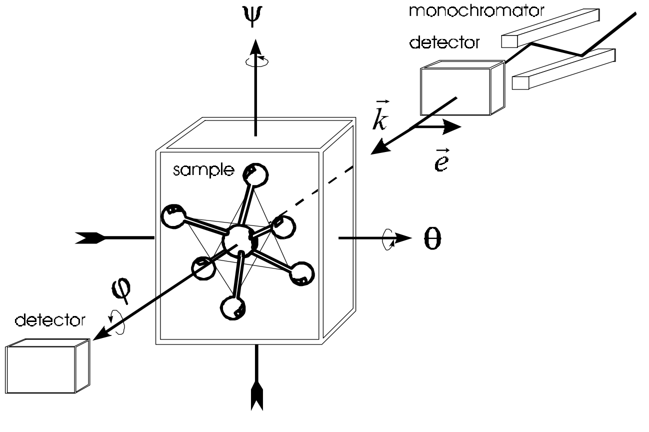

Figure 1
Scheme of experimental arrangement. A deformed octahedral cluster in the single-crystal sample is shown for its (0,0,0) position.

3. Theory

Starting with the basic formula for K-absorption (Brouder, 1990)

$$\mu(\hbar\omega,\vec{e},\vec{k}) \propto \delta(E_f - E_i - \hbar\omega)\sum^{l,m}\left(\left|\left\langle R_l\, Y_{lm}\left|\,\vec{e}\cdot\vec{r}\,\right|R_{10}Y_{00}\right\rangle\right|^2 + \frac{1}{4}\left|\left\langle R_l Y_{lm}\left|\,\vec{e}\cdot\vec{r}\vec{r}\cdot\vec{k}\,\right|R_{10}Y_{00}\right\rangle\right|^2\right) \tag{1}$$

and inserting the mathematical expressions for the angular parts of the wave functions (Bocharov *et al*. 1998), one can obtain the absorption coefficient as the sum of dipole and quadrupole components $\mu = \mu_D + \mu_Q$, where

$$\mu_D \propto p_x e_x^2 + p_y e_y^2 + p_z e_z^2 \tag{2}$$

$$\mu_Q \propto d_{xy}(e_x k_y + e_y k_x)^2 + d_{xz}(e_x k_z + e_z k_x)^2 + d_{yz}(e_y k_z + e_z k_y)^2 + d_{x^2-y^2}(e_x k_x - e_y k_y)^2 + \sqrt{3} d_{z^2}(e_z k_z)^2 .$$

This means, that each polarized spectrum can be interpreted as a weighted sum of partial symmetry resolved components. Each of the components is formed only by the transitions to orbitals with a definite angular momentum. The factors $p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$, and d_{z^2} represent the so called partial spectral components, i. e. the densities of states with a definite orbital symmetry modulated by the radial transition probability. We assume the radial matrix elements are equal for all states with equal quantum number l and change with energy only insignificantly. The expressions in parenthesis in equation (2) (combined from the projections of the vectors $\vec{e}$ and $\vec{k}$ and taken in the power of two) are the coefficients of these components and are determined just by the actual experimental setting. We call these coefficients partial spectral weights.

Therefore, by measuring three spectra (each of them represented by the absorption coefficient μ) with different orientations I, II and III of vector $\vec{e}$ relative to the crystal structure, one can use the expression (2) to set up an appropriate system of linear equations and extract the partial-density components p_x, p_y, p_z:

$$\mu^I \propto p_x(e_x^I)^2 + p_y(e_y^I)^2 + p_z(e_z^I)^2$$

$$\mu^{II} \propto p_x(e_x^{II})^2 + p_y(e_y^{II})^2 + p_z(e_z^{II})^2$$

$$\mu^{III} \propto p_x(e_x^{III})^2 + p_y(e_y^{III})^2 + p_z(e_z^{III})^2$$

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \propto \begin{pmatrix} \left(e_x^I\right)^2 & \left(e_y^I\right)^2 & \left(e_z^I\right)^2 \\ \left(e_x^{II}\right)^2 & \left(e_y^{II}\right)^2 & \left(e_z^{II}\right)^2 \\ \left(e_x^{III}\right)^2 & \left(e_y^{III}\right)^2 & \left(e_z^{III}\right)^2 \end{pmatrix}^{-1} \cdot \begin{pmatrix} \mu^I \\ \mu^{II} \\ \mu^{III} \end{pmatrix}, \tag{3}$$

provided that the quadrupole contributions can be neglected. The upper indices in (3) distinguish between three independent spectra recorded for different sample orientations I, II and III.

In special cases, e.g. in cubic crystals, quadrupole d-like components can also be determined.

4. Applications

Linear dichroism in NEXAFS and EXAFS can be used to study the geometrical, electronic and magnetic structure of single-crystal solids by taking advantage of the multipole character of the X-ray transitions and the selection rules for linearly polarized and angular dependent X-ray spectra.

4.1. Geometrical structure

In the case of Near-Edge X-ray Absorption Fine Structure (NEXAFS) the information on the geometrical structure will be given by the dipole transition matrix elements $\langle \psi_f | \vec{e} \cdot \vec{r} | \psi_i \rangle$ for linearly polarized radiation and by suitable model calculations, e.g. multiple-scattering (MS) calculations (Zabinsky *et al*., 1995).

From the Extended X-ray Absorption Fine Structure (EXAFS) a detailed geometrical structure information can be obtained from the term $(\vec{e} \cdot \vec{r}_n)^2$ in the EXAFS formula ($\vec{e}$ polarization vector, $\vec{r}_n$ vector from the absorbing to the nth neighboring atom).

With the measurement and interpretation of the polarization dependent Fe K-EXAFS of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ single crystals an example for the investigation of the geometrical structure of complex ions has been given (Gaedeke *et al*., 1988).

4.2. Multipole character of X-ray transitions and electronic structure

For investigating the multipole character of X-ray transitions the different matrix elements $\langle \psi_f | \vec{e} \cdot \vec{r} | \psi_i \rangle$ for dipole transitions and $\langle \psi_f | \vec{e} \cdot \vec{r}\vec{r} \cdot \vec{k} | \psi_i \rangle$ for quadrupole transitions and the measured angular dependence of the XANES enable to distinguish between the two types of electric transitions (Brümmer *et al*., 1971; Dräger *et al*., 1988).

The orbital symmetry of empty 3d states in cubic MeO oxides could be determined using the $\vec{e}$ and $\vec{k}$ dependence of 1s→3d quadrupole transitions in the pre-edge absorption of the Me K-NEXAFS for Me = Mn, Fe, Co and Ni. The experimental technique is described elsewhere (Heumann *et al*., 1997). All determinations of empty 3d orbital symmetries agree with results of modern band structure calculations for strongly correlated materials (Terakura *et al*., 1984; Hugel & Kamal, 1996).

The orbital symmetry resolution of the V K-NEXAFS of V_2O_5 shows that the linear dichroism resulting from quadrupole transitions is small but not negligible (Sipr *et al*., 1999).

A detailed quantitative analysis of Cu K-NEXAFS of HTSC-$Bi_2Sr_2CaCu_2O_8$ for five selected sample orientations has provided the partial DOS components $p_{x,y}$, p_z, d_{z^2}, $d_{x^2-y^2}$, and d_{xy} for Cu. Here it can be emphasized (Dräger, 1996):

- the high selectivity of the method with respect to the symmetry of states,
- the localization of the Cu 3d hole preferred in the $3d_{x^2-y^2}$ orbital and
- the strong bulk sensitivity of the transmission mode which can be applied to K absorption as opposed to the surface sensitive yield modes which are usually used when measuring L absorption spectra.

The quality of band structure and real-space multiple-scattering (RS-MS) calculations for reproducing experimental 3d metal K-NEXAFS and the consideration of core-hole effects has been investigated and proved by comparison with the appropriate spectra of TiS_2, $TiSe_2$, $TiTe_2$ and V_2O_5 (Simunek *et al*., 1997; Bocharov *et al*., 1998; Sipr *et al*., 1999). A comparison of the experimental results with theoretical RS MS calculations show the sufficiency of one-electron model for the description of p-like states. The influence of core hole can be treated reasonably good within the so called “relaxed and screened approximation”. A tendency of reducing of the quadrupole contributions for the transition metal compounds is observed going from Ni to Mn.

Many crystal structures are built up of identical fragments, e.g. ionic complexes which have different orientations of their symmetry axes. This is true for the structures like monoclinic β-copper phtalocyanine (CuPc) and monoclinic CuO, which are composed by two differently oriented patterns of CuPc molecules and CuO_2 chains, respect. Therefore, unambiguous comparison of experiment and theory depends on the orientation of coordinate system in which the electronic structure calculation or spectra resolution should be performed. Especially, for comparison of experimental data with the results of MO or MS Xα-cluster calculations the spectra should be decomposed with respect to the symmetry axes of the concerned molecules or atomic clusters.

As an experimental example, Fig. 2 shows the resolution of polarized Cu K-NEXAFS of CuO into the p_x-, p_y- and p_z –like spectral components in the coordinate system of the crystal unit cell and with respect to that of a single CuO_4 cluster.

Another example is shown in Figs. 3a,b for the Cu K-NEXAFS of CuPc (Copper Phthalocyanine). Here it will be pointed to the three different p-like spectral components obtained by resolving with respect to the coordinate system of the monoclinic unit cell (Fig. 3a). On the other hand, we obtained degenerated $p_{x,y}$ -components in the coordinate system of the CuPc molecule because of its D_{4h} symmetry (Fig. 3b).

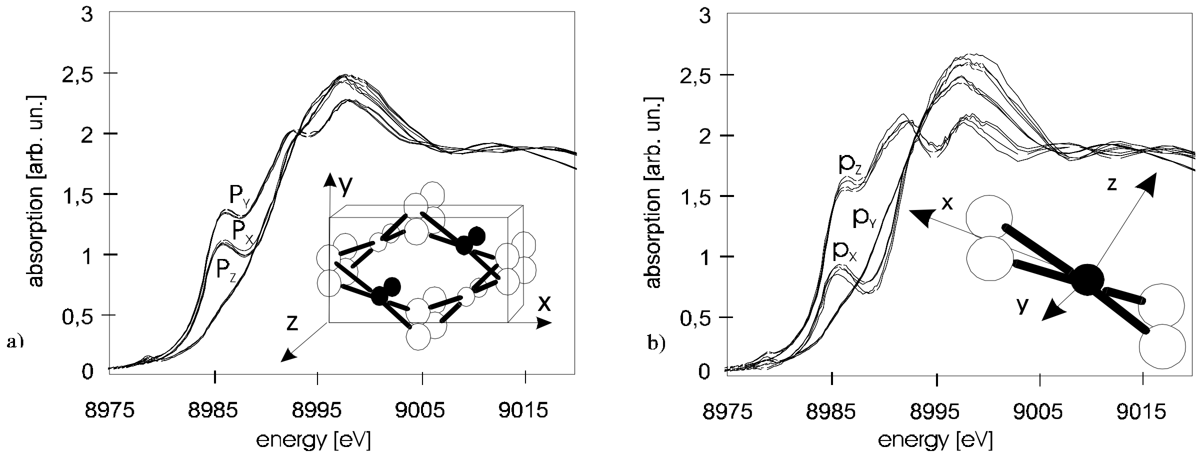

Figure 2

The Cu p-like partial spectral components of the Cu K-NEXAFS of CuO resolved with respect to the two coordinate systems shown in a) and b). Each component was obtained from four different sets of experimental spectra, represented by the respective group of curves and showing the consistence of the solutions.

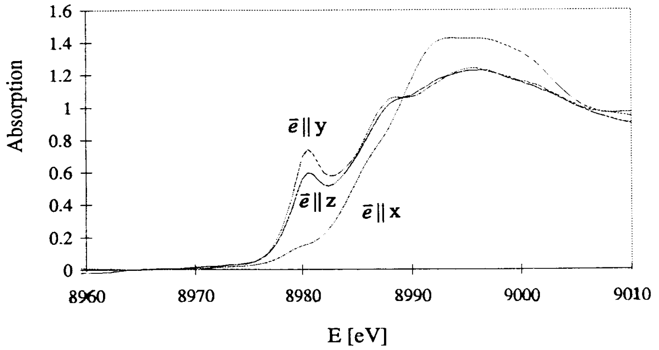

Figure 3a
Cu K-NEXAFS of CuPc resolved into spectral components with respect to the coordinate system of the crystal

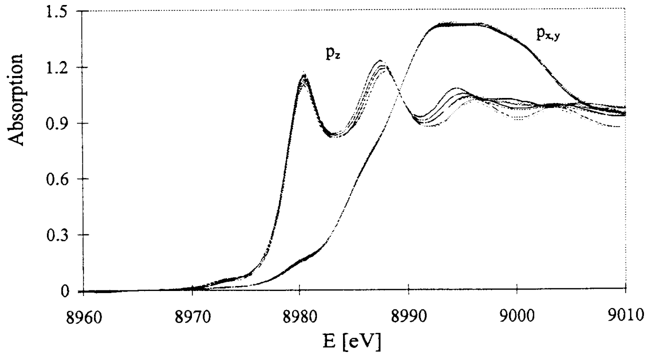

Figure 3b
Cu K-NEXAFS of CuPc resolved into spectral components with respect to the coordinate system of a planar molecule

4.3. Spin-resolved NEXAFS from RXS

Recently the authors have developed a new method for spin-resolving of NEXAFS by analysis of resonantly scattered X-ray core lines (see the contributed paper: G. Dräger et al. “Spin-resolved NEXAFS from resonant X-ray scattering (RXS)” in this proceedings). Since the method employs spin conservation and local spin references antiferromagnetic and paramagnetic materials can be investigated as well.

The experimental work was supported by Hamburger Synchrotronstrahlungslabor HASYLAB (Project No. II-99-083).

References

Bocharov, S., Draeger, G., Heumann, D., Simunek, A., & Sipr, O. (1998). Phys. Rev. B **58** (12), 7668-7674.

Brouder, C. (1990). J.Phys. C**2**, 701-738.

Bruemmer, O., Draeger, G., & Starke, W. (1971). J.Physique **32**, C4-169-171.

Dräger, G. (1996). AIP Conf. Proc. **389**, 557-568.

Dräger, G., Frahm, R., Materlik, G., & Bruemmer, O. (1988). phys. stat. sol. (b) **146**, 287-294.

Gaedeke, W., Koch, E. E., Draeger, G., Frahm, R., & Saile, V. (1988). Chemical Physics **124**, 113-119.

Heumann, D., Dräger, G., & Bocharov, S. (1997). J. Phys. IV France **7**, C2-481-483.

Simunek, A., Sipr, O., Bocharov, S., Heumann, D., & Draeger, G. (1997). Phys. Rev. B **56**(19), 12232-12237.

Sipr, O., Simunek, A., Bocharov, S., Kirchner, Th., & Draeger, G. (1999). Phys. Rev. B **60**(20), 14115-14127.

Terakura, K., Oguchi, T., Williams, A. R., & Kübler, J. (1984). Phys. Rev. B **30**(8), 4734-4741.

Hugel, J. & Kamal, M. (1996). Sol.Stat.Comm. **100**(7), 457-461.

Zabinsky, S. I., Rehr, J. J., Akudinov, A., Albers, R. C., & Eller, M. J. (1995). Phys. Rev. B **52**, 2995- 3009.

Received 31 July 2000 • Accepted 14 November 2000