| ESRF | **Experiment title:** ***X-RAY ELECTRO-OPTICS & OPTICAL ACTIVITY IN SEMICONDUCTORS WITH WURTZITE STRUCTURE*** | **Experiment number:** **HE-2548** |
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## 1. VECTOR PART OF OPTICAL ACTIVITY IN THE X-RAY RANGE

*Linear* electro-optical properties of crystals have been known for more than a century at optical wavelengths but no such effect has ever been observed with X-rays. We are interested in III-V semiconductor crystals that are *pyroelectric* and exhibit an Optical Activity (OA) tensor that has an irreducible representation which transforms in O(3) as a ***polar vector***. The conditions under which such a *polar* OA can be detected with X-rays were discussed in a recent paper[1] : this effect was observed in a single crystal of zincite (class 6mm) on recording X-ray detected *Circular Intensity Differentials* (XCID) spectra in the X-ray resonant diffraction regime near the Zn K-edge using a strong (300) reflection at Bragg angles near 45°. A first step in proposal HE-2548 was to check whether the same information could be obtained on measuring the ratio: $XCID^{(\sigma,\pi)} = [\mathbf{I}_s^{L(\sigma,\pi)} - \mathbf{I}_s^{R(\sigma,\pi)}]/[\mathbf{I}_s^{L(\sigma,\pi)} + \mathbf{I}_s^{R(\sigma,\pi)}]$ in the RIXS regime. Here, the superscripts $(\sigma,\pi)$ refer to the linear polarization of the ***inelastic scattering*** intensity $\mathbf{I}_s$ while the incident X-ray photons are either left (L) or right (R) circularly polarized. For any wurtzite-type crystal (e.g. of ZnO, GaN…) with the **c** axis oriented perpendicular to the diffraction plane whereas the crystal axes **1** and **3** taken along **a** and **c** respectively, one may expect $XCID^{(\sigma)} \propto t_{113} = Re\ [E1E2]_{113}$ in which E1E2 denotes the rank-3 tensor of interference terms between the electric dipole (E1) and electric quadrupole (E2) transition probabilities. A key property of the *polar* OA is that $t_{113}$ should change its sign if the crystal is rotated by 180° around the direction of the incident or the scattered X-ray beam.

The effective operator involved in polar OA is the *electric polarization* vector most often associated with a pyroelectric behaviour, *i.e* a spontaneous *electric* order. Let us suppose that such a ferroelectric order could be either generated or simply perturbed by an external electric field: the polar OA could then be seen as a linear electro-optical effect, the sign of which should be correlated with the direction of the electric field.

## 1. POLAR OPTICAL ACTIVITY MEASURED IN THE RIXS REGIME

For such a first test-experiment, we found preferable to re-use the same zincite crystal which we used before to detect the polar OA in the resonant diffraction regime[1]. As illustrated with Fig. 1, the geometical arrangement of the crystal was the same as for the resonant diffraction experiment: the **c** axis was set

perpendicular to the plane of incidence whereas the angle of incidence was adjusted to 45°. The main difference with our previous experiment is that the X-ray photons emitted at 90° from the incident X-ray beam were now analyzed in energy with a spherically bent Si (440) crystal analyzer. Recall that with such a crystal analyzer, the Bragg angle is either 48.37° or 48.55° for the fluorescence $K\alpha_1$ & $K\alpha_2$ lines of zinc.

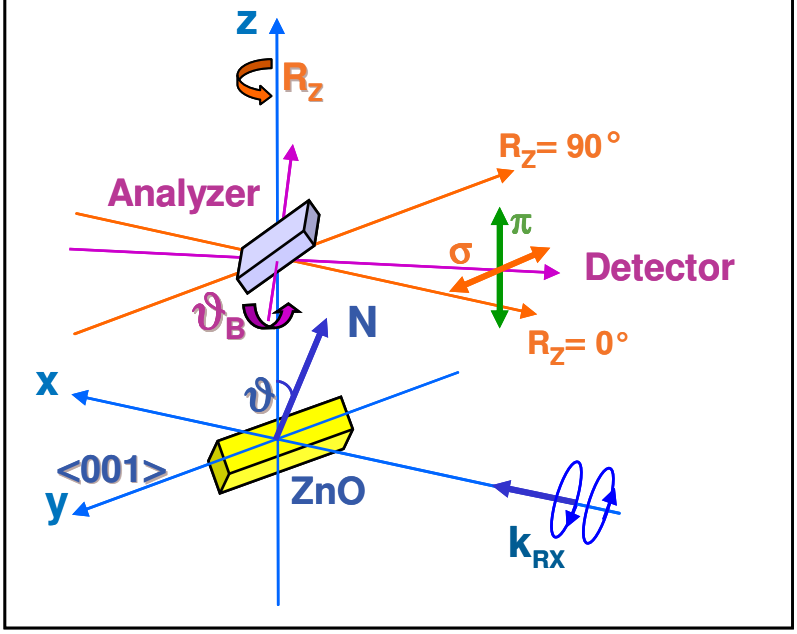


Figure 1

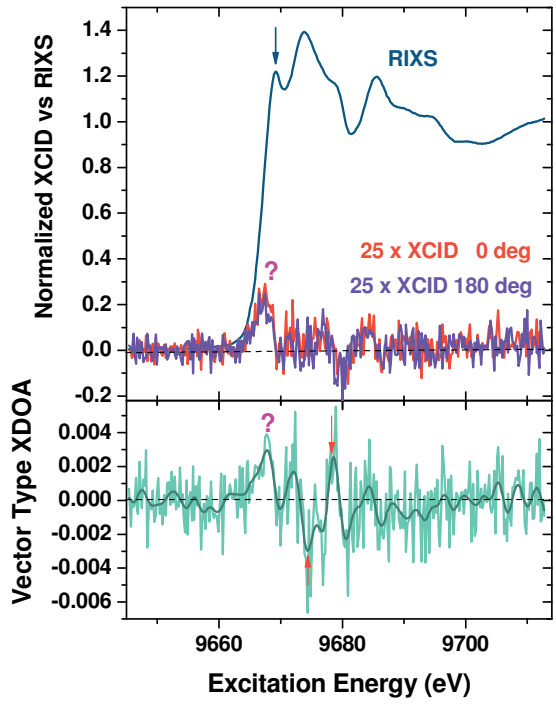


Figure 2

The results are illustrated with Figures 2. High quality RIXS spectra (photon-in, photon out) were recorded at the Zn K-edge with the analyzer tuned to the energy of the Zn $K\alpha_1$ line. Note that the shoulder marked with an arrow is nicely resolved whereas this is not the case for excitation spectra recorded on collecting the *integrated* fluorescence on a photodiode. The XCID spectra recorded for two opposite directions (0°;180°) of the crystal **c** axis were unexpectedly weak. Indeed, the difference signal obtained from these two XCID is also very weak. There is, however, no ambiguity that this spectrum contains a weak contribution of the expected polar XDOA signal which is peaking at strictly the same energies (marked with arrows) as in the XDOA spectra recorded previously using resonant diffraction[1]. Unfortunately, since the XDOA signal is very weak and the RIXS data acquisition time is very long, we cannot exclude that the spectrum could be contaminated (near the rising edge) with a weak residual RIXS derivative signal as suggested with a question mark.

The important point which still deserves to be clarified is to understand why the XDOA signal measured in RIXS geometry is much weaker than the signal measured in resonant diffraction. It is quite clear that such a polar XDOA signal cannot be measured in *absorption* and, therefore, one should have anticipated that this signal should not show up in the integrated *fluorescence* emission that arises from the relaxation of the deep core hole. In contrast, the polar XDOA signal should contribute to the *Resonant Raman Scattering* (RRS) process which, inherently, does not depend on the life time of any virtual core hole. To the best of our knowledge, there is no way to discriminate experimentally between the two processes, …except (perhaps) on measuring the intensity of the polar XDOA signal. Unfortunately, such experiments proved to be extremely time-consuming and we had to give up with the challenging idea to detect in this way any electro-optical effect in the X-ray range. In conclusion, resonant X-ray diffraction remains the only practicable option to exploit the information content of the polar XDOA signal. Future projects on ID12 will thus concentrate on that option.

**REFERENCE**

[1]J. Goulon, N. Jaouen, A. Rogalev, F. Wilhelm, Ch. Goulon-Ginet, Ch, Brouder, Y. Joly, E. Ovchinnikova, and V. Dmitrienko, *Vector part of optical activity probed with x-rays in hexagonal ZnO.* *J. Phys : Condens Matter* **19**, (2007), 156201 (18pp).