Extraction of Electron Magnetic Circular Dichroism from Energy-Filtered Nano-Diffraction by Multivariate Curve Resolution Technique

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Electron magnetic circular dichroism (EMCD) is a transmission electron microscopy analogue of better known x-ray magnetic circular dichroism (XMCD). Both techniques are based on an element-selective excitation of a core electron into unoccupied valence states. Transmission electron microscope (TEM) brings an additional advantage of a superior lateral resolution, which reaches in principle sub-Angstrom range [1].

Despite an intense initial activity in EMCD, the experiments are still primarily in the method development stage. The main reasons are high demands on quality of sample preparation, low signal to noise ratio and complications due to dynamical diffraction effects. So far one can obtain the best control over signal to noise ratio by measuring energy-filtered electron diffraction datacubes. Once one has a matrix of spectra, it can be processed independently one-by-one to provide a rich statistics for error control [2].

The complications due to dynamical diffraction lead to a requirement to measure in a 2-beam or 3-beam crystal orientation [2]. We demonstrate how to overcome the requirement and extract the EMCD signal from arbitrary crystal orientation. The method is based on advanced statistical techniques, namely the multivariate curve resolution (MCR). The present multivariate analysis is based on the MCR-alternating least-square algorithm, whereby we adopted a faster, accurate and more robust algorithm, called the non-negative matrix factorization [3].

As a benchmark system we chose a bcc iron crystal. The electronic structure was calculated in density functional theory with local density approximation using the code WIEN2k [4]. Based on that, we calculated the mixed dynamic form factors (MDFFs) [5]. The dynamical diffraction effects were treated using the Bloch's wave formalism. We have calculated datacubes in a slightly misoriented 3-beam orientation so that the extraction of the EMCD signal would be non-trivial. We chose an orientation with an excited Bragg spot G = ±(200) for the 3-beam case. The energy-filtered diffraction patterns span an area from -1.2G to 1.2G along the systematic row and from -0.7G to 0.7G in the perpendicular direction, with step 0.025G in both directions. The resulting datacube has an energy range from 685 eV to 735 eV with step 0.05 eV. Sample thicknesses were chosen as 10 nm, 20 nm, 30 nm and 40 nm.

On top of the $L_{2,3}$ signals, we added a double-step background signal modeled as a sum of two step functions positioned at 708 eV and 721 eV, respectively. The relative intensity of the post-edge background signal was fixed to 1/3 of the intensity of the broadened nonmagnetic part of the L_3 edge peak. Finally, we also created datacubes with a Poisson noise at several noise levels. In particular, we have scaled the datacubes so that the L_3 peak intensity I_{max} at the transmitted beam has values 1000 and 10000, respectively. This allowed us to check the performance of MCR at different noise levels.

We show in the top row of Figure 1 theoretical energy integrals of the EMCD at L_3 edge and the color bar range is relative to the transmitted beam intensity at L_3 edge. We can see that the overall intensity of the EMCD signal decreases with thickness and the pattern of its distribution becomes more complicated due to stronger dynamical diffraction effects at larger thicknesses. The maximum intensity of EMCD signal reaches around 0.3% of the transmitted beam intensity.

The MCR procedure produced stable fits for all 12 tested datacubes. Every such fit results in isolation of two spectral components along with maps of corresponding positive coefficients throughout the diffraction plane. The distribution of the EMCD signal is then obtained as a difference of coefficients of the two spectral components. These maps are summarized in rows 2, 4 and 6 of Fig. 1 for noise-free, $I_{\mathrm{max}} = 10^4$ and $I_{\mathrm{max}} = 10^3$ datacubes, respectively. These maps can be compared to theoretical relative dichroic maps shown in the top row and an excellent agreement is found. The only differences are due to noise, but the position and shape of regions of positive or negative magnetic signal is recovered with high accuracy. A more quantitative measure of the quality of the fit is expressed in terms of maps of residual.

In quantitative EMCD experiments, the EMCD spectrum is analyzed by sum rule expressions in order to extract the ratio of orbital to spin magnetic moment [6]. We will apply these sum rules as a sensitive test of the accuracy of EMCD spectrum extraction. The sum rules state

$$\frac{m_l}{m_s} = \frac{2}{3}\frac{\int_{L_3}\Delta\sigma(E)dE + \int_{L_2}\Delta\sigma(E)dE}{\int_{L_3}\Delta\sigma(E)dE - 2\int_{L2}\Delta\sigma(E)dE} = \frac{2q}{9p-6q}, \quad (1)$$

where q is an energy integral of EMCD over both edges and p is an energy integral over the L_3 edge only. Without loss of generality we can rescale the EMCD spectrum or its integral so that $p = 1$. Then the orbital to magnetic moment ratio m_l/m_s, is a function of q only, allowing easy visual comparison of the energy integrals in the post-edge region. Fig. 2 summarizes the quantitative analysis of the EMCD spectra extracted by MCR method. For the noiseless datacube we obtain a value of $q = 0.120$ with a spread of less than 0.001, leading to a value $m_l/m_s = 0.029$, containing the systematic error originating from the post-edge normalization. For the noisy datacube with $I_{\max} = 10^4$ we obtained the m_l/m_s ratio ranging from 0.019 to 0.036.

The main advantage of MCR method is its generality; it does not require presence of any symmetry planes. The MCR method is therefore applicable in any geometry, not only in the near-3-beam orientation. In principle, by use of MCR method we avoid the obstacles caused by dynamical electron diffraction. Our results will simplify future analyses of the experimental EFTEM datacubes and extraction of the EMCD spectra. Experimental verification will be presented.

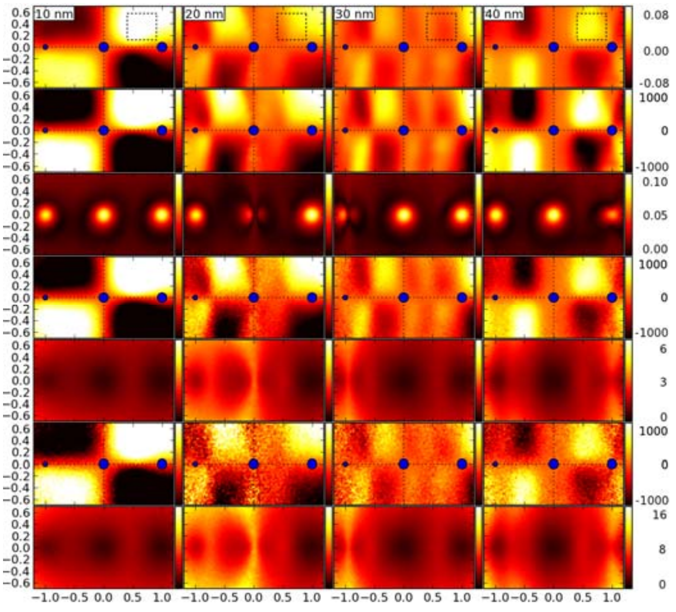

FIG. 1. Maps of distributions of EMCD signal and residui of MCR fits. See text for detail.

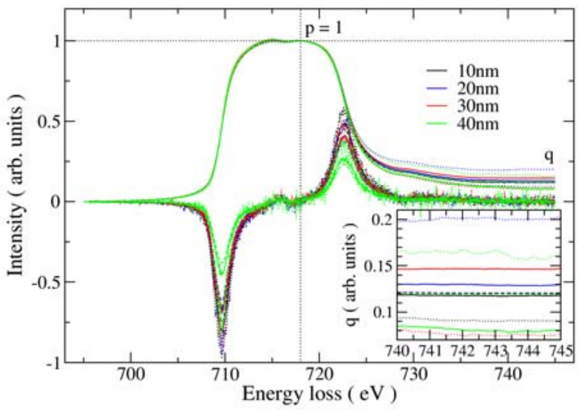

FIG. 2. EMCD spectra and their energy integrals of bcc iron crystal at 4 different thicknesses obtained by the MCR method.

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