

X-ray Natural Optical Activity beyond Chirality

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Abstract

While optical activity in achiral space groups was predicted by Gibbs as long ago as 1882 [1], linear and circular birefringence effects hamper the measurement of circular dichroism in the UV-vis energy ranges [2]. We have used tender X-rays at the ESRF beamline ID12 to examine Natural Circular Dichroism (XNCD) [3] at the K-edges of copper and iron coordination salts respectively belonging to the achiral, but optically active, point groups D_2d and S_4 . The angular dependence of the XNCD signals was revealed with respect to the polar axis, theta, as well as the azimuthal axis, phi, by careful orientation of millimetric-sized crystals in the X-ray beam. In the case of D_2d , the XNCD followed the expected angular dependence in theta and phi [3]. However, for S_4 , an offset of about 27° in phi was observed and the more complicated angular dependence was ostensibly not respected. This result was subsequently confirmed using Resonant Inelastic X-ray Scattering-NCD at the SOLEIL synchrotron, in the first example of this RIXS-NCD technique, and can be rationalized using symmetry arguments.

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