X-FEL study of charge-transfer driven by ultrafast spin-transition in a CoFe Prussian blue analogue

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Photoinduced charge-transfer is an important process in nature and technology, responsible for the emergence of exotic functionalities, like magnetic order for cyanide-bridged bimetallic coordination networks [1]. Despite its broad interest and intensive developments, an atomic-scale description of the process, coupling intermetallic charge-transfer and spin-transition, has been debated for decades and was beyond reach due to its extreme speed [2]. We study this process in a prototype cyanide-bridged CoFe system by femtosecond X-ray and optical absorption spectroscopies, allowing for disentangling ultrafast electronic and structural dynamics. Our results demonstrate that it is the spin-transition that occurs first within ≈50 fs, which drives the subsequent Fe-to-Co charge-transfer within ≈200 fs. This study represents a first step for understanding and controlling by light charge-transfer-based functions. We also studied The RbMnFe Prussian blue analogue [1] is a photoactive material for which the parameter ϒ describing the fraction of intermetallic charge-transfer (CT) couples to a structural symmetry breaking order parameter η due to the ferroelastic Jahn-Teller distortion. We study by time-resolved x-ray diffraction the response of the lattice induced by ultrashort laser excitation and report two sequential out-of-equilibrium lattice dynamics: the initial anisotropic deformation due to local structural trapping and the transient volume equilibration controlled by the long-lived photoinduced fraction of less-bonding CT state.

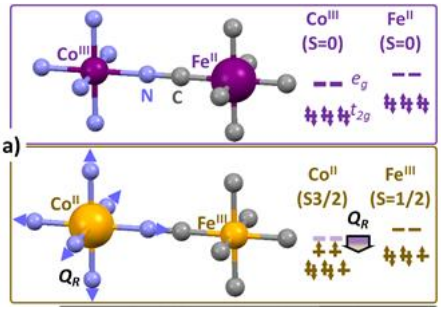

Figure 1: The cyanide-bridged coordination network with a schematic representation of the $Co^{III}(S=0)Fe^{II}(S=0)$ and $Co^{II}(S=3/2)Fe^{III}(S=1/2)$ states, where the CT is accompanied by a spin transition on the Co. The black arrows indicate that upon filling up of the e_g orbitals the Co-N distance increases (Q_R mode), which closes the Fe(t_{2g})-Co(e_g) gap as indicated by the colored arrow.

References:

[1] S. Ohkoshi, H. Tokoro, E. Collet Compte Rendus Chimie, 22 498-507 (2019)
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