Revealing charge anisotropies in metal compounds
via high-purity x-ray polarimetry

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Linear polarization analysis of hard x-rays is employed to probe electronic anisotropies in metal-containing complexes with very high selectivity. We use the pronounced linear dichroism of nuclear resonant x-ray scattering to determine electric field gradients in an iron(II) containing compound as they evolve during a temperature-dependent high-spin/low-spin phase transition. This method constitutes a novel approach to analyze changes in the electronic structure of metal-containing molecules as function of external parameters or stimuli. The polarization selectivity of the technique allows us to monitor defect concentrations of electronic valence states across phase transitions. This opens new avenues to trace electronic changes and their precursors that are connected to structural and electronic dynamics in the class of metal compounds ranging from simple molecular solids to biological molecules.

The knowledge of charge distributions and their anisotropies in molecules is crucial for understanding and precise modeling of molecular interactions and optical properties of chemical systems [1]. Powerful spectroscopic methods to investigate charge anisotropies in molecules are optical linear dichroism and birefringence that rely on probing the orientation dependence of the interaction of linearly polarized light with matter [2]. For example, optical linear dichroism is applied to follow the orientation or reorientation of molecular systems resulting from external stimuli, like any reaction that involves changing the structure or length of a molecule or structural phase transitions in molecules [3, 4]. For a microscopic analysis of charge distributions in molecules, however, one needs to apply optical techniques capable of probing atomic length scales.

The availability of highly brilliant synchrotron radiation sources has facilitated the transfer of linear and circular dichroism to the regime of hard x-rays [5, 6]. Today, x-ray linear and circular dichroism are very powerful techniques to probe charge and spin order in condensed matter with elemental specificity and site selectivity [7, 8]. Dichroic spectroscopies probe the imaginary part of the anisotropic index of refraction n by comparing the incoherent absorption of two orthogonal polarization states. The same information is also contained in the real part of n that leads to a rotation of the plane of polarization when two orthogonal polarization components experience different coherent phase shifts, an effect well known as optical birefringence. The analysis of birefringence in the x-ray regime, however, is much less common than x-ray dichroism, because efficient polarization analysis at energies of hard x-rays requires some significant technical effort. On the other hand, it opens a series of advantages compared to dichroism, because (a) it can be combined with momentum-resolving methods for high spatial resolution, (b) it does not require two subsequent measurements with different polarization states which allows for time-resolved measurements, e.g., in pump-probe schemes and (c) it promises to obtain significantly higher signal-to-noise ratios.

Recently, high-purity polarimetry in the x-ray regime has been shown to be a very sensitive technique to detect tiny changes in the polarization state of x-rays caused by the interaction with an anisotropic or chiral, thus optically active medium [9]. The technique relies on the application of x-ray linear Bragg polarizers in a 90° crossed setting with purities in the range of 10−10−10 [10]. This method is most sensitively applied at atomic absorption edges [11–13] or nuclear resonances [14–19].

Here we employ polarization-resolved nuclear forward scattering (PR-NFS) of synchrotron radiation at the 14.4-keV nuclear resonance of 57Fe to probe atomic charge anisotropies in a metal compound. If the charge anisotropy in the system leads to an electric field gradient (EFG) at the 57Fe nucleus, nuclear states with a finite electrical quadrupole moment are subject to an electric hyperfine interaction. As a result, the excited nuclear state of 57Fe splits into two sublevels, shown in Fig. 1b, which leads to a pronounced optical activity in the vicin-
Orientation dependent NFS and PR-NFS experiments at various temperatures were performed with the sample mounted on a Eulerian Cradle for angular orientation,
see Fig. 1c, whereby the cooling of the sample down to temperatures in the range of 100 K was performed by the use of a N\textsubscript{2} cryogenic gas stream [31]. A series of NFS time spectra of the SCO compound were taken at room temperature without polarization analyzer for selected orientations of the sample to confirm the magnitude of the quadrupole splitting (\(\Delta E_Q = 2.58 \pm 0.02\) mm/s, asymmetry parameter \(\eta = 0.3(\pm 0.2)\) in the Fe(II) HS state (see Supplemental Material [29], Fig. S2).

High-purity polarimetry was then performed to determine the direction of the electric field gradients in the sample. A series of PR-NFS spectra taken at \(T = 220\) K are shown in Fig. 2a. For each orientation \(\chi\), the data exhibit a temporal beat pattern resulting from a quadrupole splitting of \(\Delta E_Q = 2.64 (\pm 0.15)\) mm/s.

In addition to the time-dependent NFS and PR-NFS spectra, the time-integrated PR-NFS signal was recorded as a function of the angle \(\chi\) while the angle \(\varphi\) was kept fix (from now on referred to as \(\chi\)-PR-NFS-scans). In Fig. 2b, such a \(\chi\)-PR-NFS-scan for \(\varphi = 0^\circ\) is shown. In accordance with the PR-NFS spectra, this \(\chi\)-PR-NFS scan exhibits a minimum at \(\chi \sim -45^\circ\), which means that at this angle the main component of the EFG is either parallel or perpendicular to the incident linear \(\sigma\)-polarization. When the sample is oriented at either \(\chi \sim 0^\circ\) or \(\chi \sim -90^\circ\), the off-diagonal elements of \(f\) are maximized. Consequently, the time-integrated \(\chi\)-PR-NFS-scan has a maximum and the time-dependent PR-

FIG. 2. (a) PR-NFS spectra recorded for selected orientations \(\chi\) of the single crystal at \(T = 220\) K and \(\varphi = 0\) (black). The red lines show theoretical calculations of the scattered amplitude assuming a pure HS state with \(\Delta E_Q = 2.64 (\pm 0.15)\) mm/s and \(\eta = 0.3(\pm 0.2)\). (b) Corresponding \(\chi\)-PR-NFS-scan with theoretical calculation (red line) showing clearly the orientation dependence of the nuclear resonant \(\sigma \rightarrow \pi\) scattering. Parameters are given in Table S1 in the Supplemental Material [29]. The deviation between the simulation and the measured data for \(\chi = -45^\circ\) is due to a spurious bunch and electronic noise.

FIG. 3. (a,d): Nuclear resonant \(\sigma \rightarrow \pi\) scattering (\(\chi\)-PR-NFS-scans) taken at temperatures \(T \geq 220\) K (a) and \(T = 120\) K (d) for selected orientations \(\varphi\). The temperature dependent change of the \(\chi\)-PR-NFS-scans proves the reorientation of the EFG upon the SCO transition from the HS to the LS state. The dashed lines are guides to the eye to trace the shift of two minima of the curves for the HS and the LS state, respectively. The figures below (b,e) display the shift of these minima as function of the rotation angle \(\varphi\), starting at \(\varphi = 0^\circ\). (c,f): Schematic representation of \([\text{Fe(PM-BiA)}_2(\text{NCS})_2]\) with the orientation of the EFG at the site of the Fe atom in the HS state (c) and the LS state (f) determined via a DFT calculation assuming \(C_2\) symmetry (black vectors). The viewing direction, which corresponds to the direction of the \(V_{yy}\) component of the HS EFG and to the \(V_{xx}\) component of the LS EFG, is along the \(c\)-axis of the single crystal. For the HS state, the red arrows show the EFG orientation as determined from the experimental data, evidenced by the solid red lines in (a). The solid red lines in (b,e) are fits according to Eq. (S3) in the Supplemental Material [29], taking the EFG orientations shown in (c,f) as configuration at \(\varphi = 0^\circ\).
The detailed analysis of these data with the use of the dynamical theory of nuclear forward scattering \cite{32,33} (solid red lines in Figs. 3a,b) yields the EFG orientation of the HS state in the molecular coordinate system (Fig. 3c) and reproduces all obtained NFS time spectra taken at room temperature (see Fig. S2, Supplemental Material \cite{29}). The EFG's main axis system of the molecular HS state determined in this way is depicted in Fig. 3c together with a main axis system calculated by density functional calculations (DFT) assuming a C$_2$ symmetry \cite{34}. Allowing a tolerance of 5° the theoretical calculation reproduces the experimentally determined EFG quite well.

At $T = 120$ K the monoclinic phase of [Fe(PM-BiA)$_2$(NCS)$_2$] should be mostly in the LS state. In fact, orientation dependent NFS data obtained at $T = 120$ K show that the majority of the iron centers are in their LS state which can be inferred from the low value of the quadrupole splitting ($\Delta E_Q = 0.63 \pm 0.02$ mm/s, see Supplemental Material \cite{29}, Fig. S3). Fig. 3d displays $\chi$-PR-NFS-scans obtained at $T = 120$ K in a $\chi$-interval from $0^\circ$ to $180^\circ$. Compared to the data in Fig. 3a, the minima of the curves shift in opposite direction with increasing angle $\varphi$ as displayed in Fig. 3e. This reflects a significant change of the EFG orientation as compared to the HS state that occurs during the SCO transition. Fig. 3f shows the result of a DFT calculation of the EFG for the LS state. The red line in Fig. 3e is a theoretical simulation considering the EFG of the DFT results as starting parameter for the analysis. While this curve qualitatively describes the measured data, deviations are clearly visible. An inspection of the PR-NFS time spectra at selected angular configurations ($\varphi, \chi$) for the two temperature regimes, shown in Fig. 4, points to the origin of these deviations, as discussed below.

In contrast to the high-temperature data in Fig. 4a, the time spectra in Fig. 4b taken at 120 K are strongly orientation dependent. While oscillations with a long period of $\sim 120$ ns at ($\varphi = 60^\circ, \chi = 0^\circ$) reflect the temporal beat pattern of the quadrupole splitting of the LS state, the oscillations with the much shorter period of $\sim 30$ ns at ($\varphi = 80^\circ, \chi = -27^\circ$) carry the signature of the HS state as in Fig. 4a. This observation suggests that at $T = 120$ K there are still iron sites in the HS state which have not undergone a spin transition to the LS state. In fact, at this particular angular position, the $\chi$-PR-NFS scan in Fig. 3d exhbits a deep minimum (black arrow), while the corresponding scan in Fig. 3a has a maximum at this position (black arrow). This means that at ($\varphi = 80^\circ, \chi = -27^\circ$) the signal from the HS majority contribution is strongly suppressed by the polarimeter, thereby enabling the selective detection of the HS minority species that are still present at $T = 120$ K. The beat patterns at the other orientations appear to be a superposition of long-period and short-period oscillation belonging to the LS and HS states. Since a signature from the HS state is clearly visible in the time spectra, it can only come from an ordered HS minority species with an EFG orientation that is different from that of the LS majority species. From the relative intensity of the HS signal in the time spectra, especially at ($\varphi = 80^\circ, \chi = -27^\circ$), we estimate a fraction of 0.05 of the HS state still present at 120 K.

Without the crossed polarizers the signal from the majority LS state would be about a factor of (0.05)$^{-1}$ = 20 larger, rendering detection of the signal from the HS minority species very difficult if not impossible. Unfortunately, an accurate determination of the EFG orientation of the LS state from the experimental data is hampered by the large number of free parameters at 120 K, as discussed in more detail in Sec. 6 of the Supplemental Material \cite{29}.

In conclusion, polarization-resolved nuclear forward scattering (PR-NFS) was used here for the first time to investigate charge anisotropies via electric hyperfine in-
teractions to gain insights into the ordering of minority phases. With the help of this novel technique it could be shown that during a first order SCO transition from a HS to a LS phase the electric field gradient tensor and thus the charge anisotropy of a HS center is not affected by the increasing amount of LS centers. The HS centers retain their charge anisotropy even when present as a minority phase of a few percent.

Such studies are facilitated by the the use of synchrotron radiation (i.e. high photon flux in small, collimated beams) with its enormous brilliance and its intrinsic linear polarization that enables one to very efficiently probe electronic anisotropies in micron-sized single crystals. Single phases of materials can be selectively investigated that would not be accessible in macroscopic polycrystalline or powder samples as typically used in conventional Mössbauer spectroscopy. PR-NFS is applicable to any Mössbauer isotope that exhibits a sizeable nuclear quadrupole moment to determine the electric field gradient at the location of the nucleus. This technique opens new avenues to trace electronic changes that are connected to structural and electronic dynamics in almost all Mössbauer-active metal-containing compounds ranging from biological molecules to solid state systems. Combined with pump-probe techniques our approach opens new perspectives to reveal electronic dynamics of nonequilibrium states in molecular systems that are created, e.g., by impulsive external stimuli like temperature, pressure or electromagnetic and optical pulses: Monitoring the transmission of the polarimeter in a fixed angular setting $(\varphi, \chi)$ could reveal the emergence of electronic order in selected anisotropy directions that are transiently populated during dynamical processes. In general, our method has the potential to sensitively detect ordering phenomena at the onset of phase transitions, transient phenomena, or evolution of nonequilibrium states.

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