Figure S1. The k^3-weighted polarized Mn EXAFS spectra. Inset shows the crystal setting with respect to the incident X-ray **e**-vector and the two rotation axes, $\phi_{crystal}$ and $\chi_{crystal}$. The solid line (red), X-ray **e**-vector parallel to the crystal b-axis ($\phi_{crystal}$ = 90°, $\chi_{crystal}$ = 0°); dotted line (green), X-ray **e**-vector parallel to the c-axis ($\phi_{crystal}$ = 0°, $\chi_{crystal}$ = 0°); dash-dot line (blue), X-ray **e**-vector parallel to the a-axis ($\phi_{crystal}$ = 0°, $\chi_{crystal}$ = 90°).
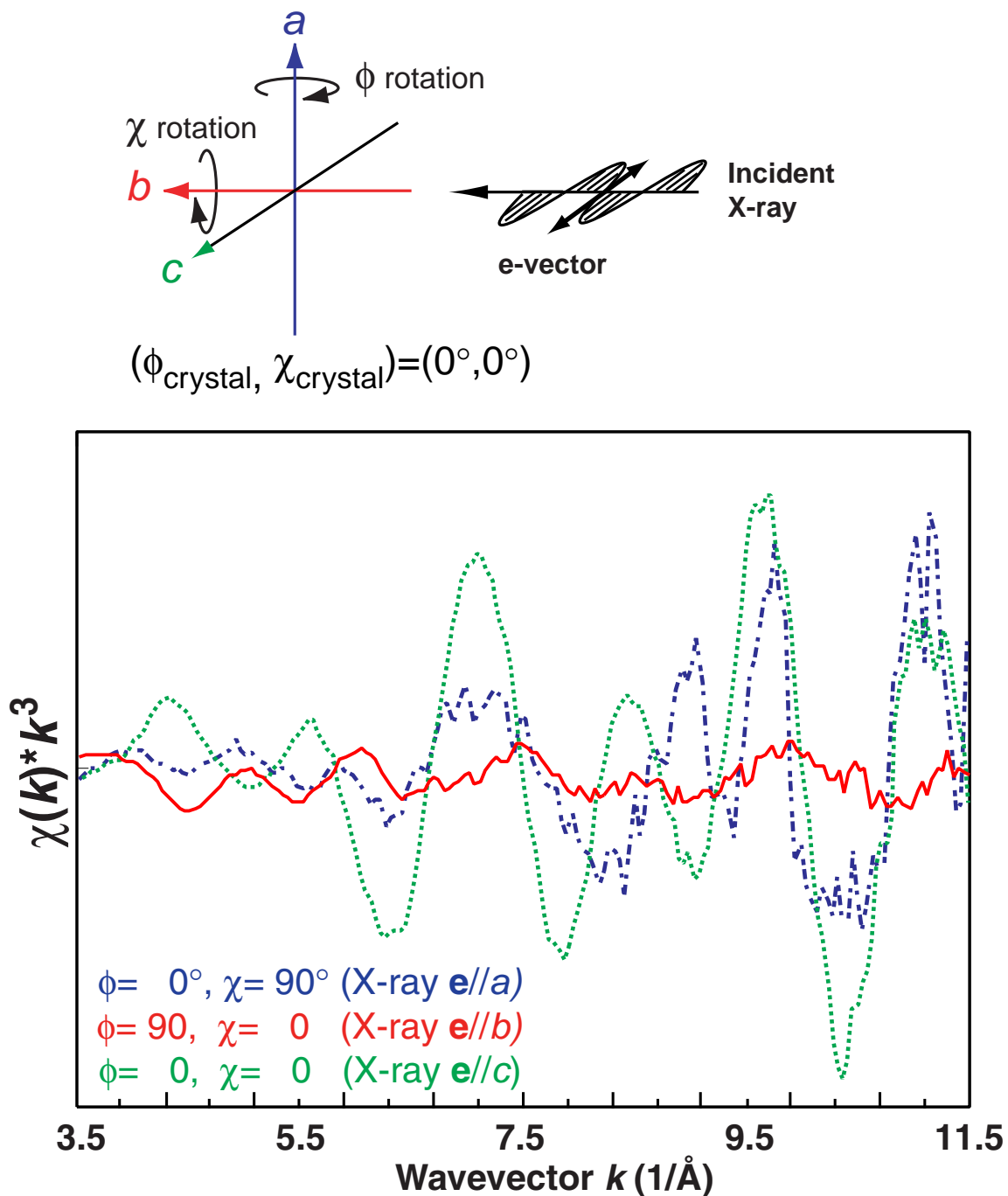
Figure 2S. Fourier transforms of the k^3-weighted polarized Mn EXAFS spectra. The solid line (red), X-ray **e**-vector parallel to the crystal *b*-axis ($\phi_{crystal} = 90°$, $\chi_{crystal} = 0°$); dotted line (green), X-ray **e**-vector parallel to the *c*-axis ($\phi_{crystal} = 0°$, $\chi_{crystal} = 0°$); dash-dot line (blue), X-ray **e**-vector parallel to the *a*-axis ($\phi_{crystal} = 0°$, $\chi_{crystal} = 90°$). At ($\phi_{crystal}$, $\chi_{crystal}$) = (0°, 0°), the Mn-Mn vector (at ~2.7 Å, the second Fourier peak) amplitude was maximal, while it was close to the noise level at ($\phi_{crystal}$, $\chi_{crystal}$) = (90°, 0°) orientation. The Mn-ligand vector amplitude at ~2 Å was also minimal at the ($\phi_{crystal}$, $\chi_{crystal}$) = (90°, 0°) orientation.