ESRF	**Experiment title:** Dispersive 4*f* crystal field excitations in rare-earth intermetallics probe by resonant inelastic x-ray scattering	**Experiment number**: HC 672
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Report:

Aim of the experiment was to demonstrate that soft X-ray RIXS at the $M_{4,5}$ edges of the rare-earths can be used to probe crystal electrical field (CEF) excitations of the 4*f* shell. In particular, we wanted to use the high momentum resolution of RIXS to verify that the CEF excitation energies within a 4*f* multiplet can become **Q** dependent when hybridizing with itinerant valence states.

In the first part of the experiment we tried to show that spin-orbit (SO) excitations between multiplets with different *j* and CEF field excitations within the same 4*f* multiplet can indeed be seen with RIXS. To this end, we decided to start our experiment on the simplest possible 4*f* configurations with either zero or one electron in the 4*f* shell, i.e. $4f^0$ and $4f^1$. These configurations are easy to model theoretically and are, therefore, best suited for our purposes. For the $4f^0$ configuration, no electronic excitation within the 4*f* shell can take place during the RIXS process and apart from *d-f* charge-transfer excitations at several eV excitation energy the scattering should be purely elastic. In the $4f^1$ configuration both electronic excitations from the $^2F_{5/2}$ ground state multiplet to the $^2F_{7/2}$ ground state multiplet can occur (SO or *jj* excitation). Furthermore, if split by a CEF the degeneracy of the two multiplets is partly or entirely lifted, given rise to further fine structure in the excitation spectrum, due to possible excitations between the CEF levels (CEF excitations). All

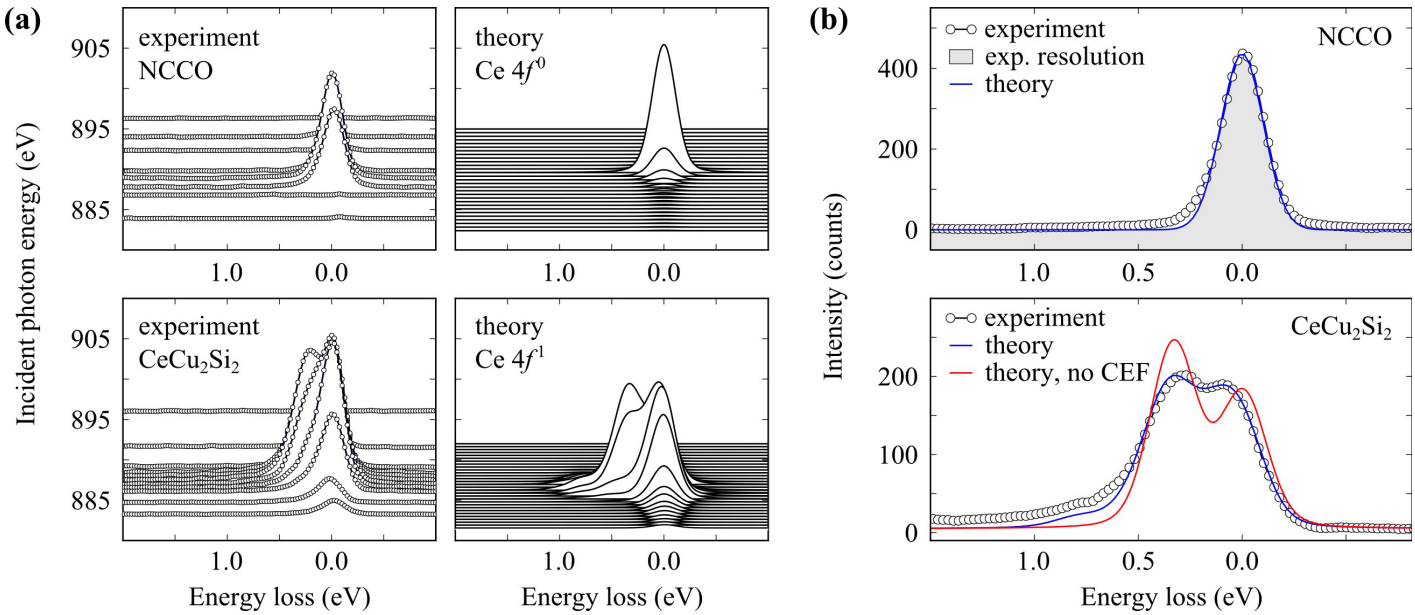

Figure 1: (a) *Experimental RIXS data taken from NCCO (Ce^{4+}, $4f^0$) and CeCu2Si2 (Ce^{3+}, $4f^1$) across the Ce M_5 edge compared with results of atomic multiplet calculations for the corresponding 4f shell configurations.* ***(b)*** *Detailed comparison of the experimental excitation spectra in the white line of the absorption edge with the the calculated spectra. The CEF parameters for $CeCu_2Si_2$ have been taken from inelastic neutron scattering results reported in [Phys. Rev. B **47**, 14280].*

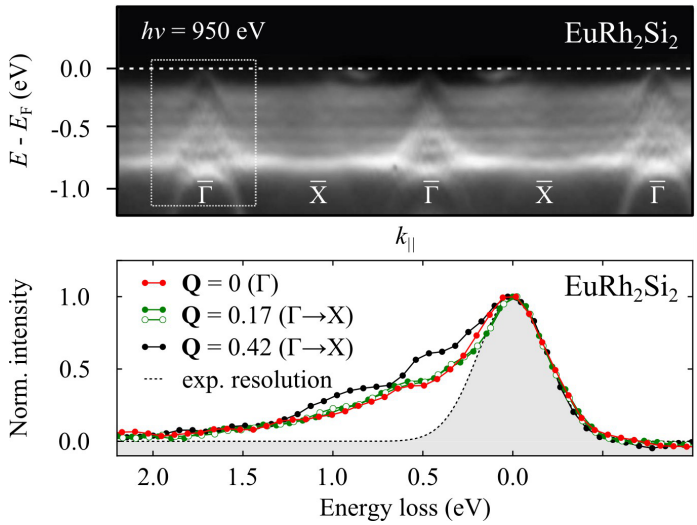

Figure 2: *Momentum dependence of the CF levels in $EuRh_2Si_2$ seen in ARPES and* ***Q*** *dependent RIXS measurements of the CF excitations.*

measured compounds have the same space group, I4/mmm, which was chosen because the corresponding CEF with D_{4h} symmetry fully lifts the degeneracy of the 4*f* multiplets.

Fig. 1a shows the excitation spectrum at the Ce M_5 edge for the two compounds $Nd_{0.86}Ce_{0.14}CuO_4$ (Ce $4f^0$) and $CeCu_2Si_2$ (Ce $4f^1$) as a function of incident photon energy. As expected, the scattering of the Ce $4f^0$ system is purely elastic while the excitation spectrum of $CeCu_2Si_2$ has strong inelastic contributions. Atomic multiplet calculations can nicely reproduce the experimental data. It should be noted that in the case of $CeCu_2Si_2$, i.e. Ce $4f^1$, a good agreement is only achieved when including both SO and CEF excitations in the calculations (Fig. 1b). These results unambiguously confirmed that SO and CEF excitations in the 4*f* shell of rare earth ions can be probed with RIXS, although the limited energy resolution prevents resolving the transitions between the 7 Kramers doublets individually.

Animated by these results, we started looking for signs of a momentum dependence in the CEF excitations. To this end, we changed samples and used the Eu compound $EuRh_2Si_2$ ($4f^7$) for which we have seen a strong **k** dependence of the CEF levels around the $\bar{\Gamma}$ point of the Brillouin zone in angle-resolved photoemission spectroscopy (ARPES). Note that RIXS measurements at the Eu edge are more challenging both experimentally, because the ID08 spectrometer is optimized for lower energies around the Ce edge, and theoretically, because of the huge number of possible intermediate and final states. However, to demonstrate a **Q** dependence of the CEF excitations we consider them as most suitable. The CEF splittings are the largest among the rare-earths and the dispersion of the CEF levels is seen in the center of the BZ which makes and alignment of the samples in the experiment very easy. In Fig. 2 we show the excitation spectrum of $EuRh_2Si_2$ for different **Q** along the $\bar{\Gamma}$-$\bar{X}$ direction together with our previous ARPES results. Moving away from the $\bar{\Gamma}$ point we see notable changes in the excitation spectrum. In particular, the energy position of some spectral features shifts with **Q** which is a strong indication of a momentum dependence of the CEF excitations. A detailed analysis of the spectral features is currently under way.

In summary, we have demonstrated that SO and CEF excitations in the 4*f* shell of the rare earths can be seen using RIXS at the $M_{4,5}$ edges. Furthermore, we have observed strong indications of a **Q** dependence in the CEF excitations. A severe limitation is the rather poor energy resolution which prevented us from resolving the individual excitations. It would be extremely insightful if our measurements were repeated with considerably higher energy resolution.