High multipole transitions in NIXS: Valence and hybridization in 4f systems


1 Department of Physics, Simon Fraser University - Burnaby, BC, V5A 1S6, Canada
2 Department of Physics, University of Washington - Seattle, WA, 98105, USA
3 II. Physikalisches institut, Universität zu Köln - Zülpicher Str. 77, D-50937 Köln, Germany
4 Department of Physics and Astronomy, University of British Columbia - Vancouver, BC, V6T 1Z1, Canada
5 Department of Quantum Matter, ADSM, Hiroshima University - Higashi-Hiroshima 739-8530, Japan
6 Department of Chemistry, University of Western Ontario - London, Ontario, N6A 5B7, Canada

received 10 October 2007; accepted in final form 19 November 2007
published online 7 December 2007

PACS 61.05.cf – X-ray scattering (including small-angle scattering)
PACS 78.20.Bh – Theory, models, and numerical simulation
PACS 61.05.cj – X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc.

Abstract – Momentum-transfer (q) dependent non-resonant inelastic X-ray scattering measurements were made at the N_{4,5} edges for several rare-earth compounds. With increasing q, giant dipole resonances diminish, to be replaced by strong multiplet lines at lower energy transfer. These multiplets result from two different orders of multipole scattering and are distinct for systems with simple 4f^0 and 4f^1 initial states. A many-body theoretical treatment of the multiplets agrees well with the experimental data on ionic La and Ce phosphate reference compounds. Comparing measurements on CeO_2 and CeRh_2O_4 to the theory and the phosphates indicates sensitivity to hybridization as observed by a broadening of 4f^0-related multiplet features. We expect such strong, non-dipole features to be generic for NIXS from f-electron systems.

Copyright © EPLA, 2008

The electronic, magnetic, and structural properties of rare-earth materials are strongly influenced by intra- and inter-atomic interactions involving the 4f electrons. The problem of the local electronic structure of Ce provides a valuable case in point. Both Ce^{3+}(4f^1) and Ce^{4+}(4f^0) formally exist in ionic materials, but interaction between the 4f states and ligand or conduction states plays an important role in many-valence fluctuation or heavy-fermion cerium materials [1–11] such as Ce metal, CeRh_2, CePd_3, and CeO_2, with cerium oxides in particular continuing to attract considerable attention for their catalytic properties [12–16]. The importance of hybridization in spite of the small radial extent of the 4f wave functions is due to the large 4f degeneracy. Further understanding of the 4f localization behavior in this class of materials is hampered not only by the theoretical difficulties presented by, e.g., competing interactions and strong hybridization, but also by the difficulty in obtaining and interpreting relevant spectroscopic information about the Ce local electronic structure.

Several core-shell spectroscopies have been applied to the 4d initial state in order to probe f-type final states in cerium compounds. At the Ce N_{4,5} edge, spin-orbit splitting is small, 4f-4d interaction is large [7], and the low binding energy of the 4d states compared to 3d or 2p orbitals results in a core-hole whose effect on 4f energy levels from reduced screening of the nuclear charge is lessened. X-ray absorption spectroscopy (XAS) measurements at the N_{4,5} edge however, contain both surface and bulk effects in their results and the need for a bulk-sensitive probe is understood [1]. Weak pre-edge multiplet features observed by XAS [4,6,8–10,17] at the N_{4,5} edge are due to the slight mixing of localized dipole-forbidden and delocalized dipole-allowed states [17]. Reflection-mode electron energy loss spectroscopy (EELS) at low incident electron energy has also been used to probe dipole and non-dipole transitions to 4f-type final states [18,19], but such measurements are also quite surface sensitive and may have additional complications due to multiple scattering.

We revisit the phenomenon of excitations at the N_{4,5} edge in cerium compounds from a new perspective: non-resonant inelastic X-ray scattering (NIXS) [20,21]. Unlike
XAS or electron spectroscopies at this edge energy, the fact that both the incident and scattered photons are relatively high energy (typically \( \sim 10\text{keV} \)) ensures that NIXS is an inherently bulk-sensitive technique [22,23]. We find that \( q \)-dependent NIXS provides straightforward, bulk-sensitive measurement of both dipole-allowed and dipole-forbidden \( 4d \rightarrow 4f \) transitions in Ce compounds. Doing so has revealed strong pre-threshold resonances that are non-dipole in character, sensitive to \( f \)-occupation, and dominate the spectrum at high \( q \).

The double-differential cross-section in a NIXS measurement [24,25] is

\[
\frac{d^2\sigma}{d\Omega d\omega} = \left( \frac{d\sigma}{d\Omega} \right)_T S(q, \omega),
\]

where \((d\sigma/d\Omega)_T\) is the Thomson scattering cross-section and \(S(q, \omega)\) is the dynamical structure factor. Note that

\[
S(q, \omega) = \sum_f \left| \langle f | e^{i \mathbf{q} \cdot \mathbf{r}} | i \rangle \right|^2 \delta(E_i - E_f + \hbar \omega),
\]

where \( q \) is the momentum transfer, \( \mathbf{k}_f - \mathbf{k}_i \), and \( \hbar \omega \) is the photon energy loss. When \( q(\mathbf{q}) \) is sufficiently small, the matrix element reduces to a dipole transition as is the photon energy loss. When \( \mathbf{q} \) is sufficiently large, the contribution to the spectrum from the dipole resonance is heavily diminished and the growth of a new multiplet structure manifests as higher-order (\( i.e. \) beyond dipole) transitions begin to contribute. Note that the multiplet features arrive with two different \( q \)-dependencies, indicating the presence of two different non-dipole scattering channels. This is well illustrated by the La compound. At 3.9 \( \text{Å}^{-1} \), two peaks have emerged 13eV and 16eV below the giant resonance. At 7.7 \( \text{Å}^{-1} \), additional features begin to appear \( \sim 15\text{eV} \) and 18eV below the giant resonance. By \( q \sim 8\text{Å}^{-1} \), the contribution to the spectrum from the dipole resonance is heavily reduced [25,39] and the NIXS spectra near the 4d binding energy are dominated by the pre-threshold structure. These results show a strong sensitivity of the non-dipole multiplet structure to the 4f occupation. As the final states for these transitions are apparently localized (given their discrete nature), we infer that the non-dipole transitions are atomic-like \( 4d^{10}4f^{n-1} \rightarrow 4d^{10}4f^{n+1} \) of differing symmetry (\( e.g. \), \( 1S \rightarrow 1F \), octupole; \( 1S \rightarrow 1H \), triakontadipole; etc) and that the different multiplet spectra represent the difference between \( 4f^{0}(\text{La}^{3+}) \) and \( 4f^{1}(\text{Ce}^{3+}) \) initial states.

Calculations of the NIXS spectra at the Ce \( N_4 \) edge were performed for the two ionic configurations \( \text{Ce}^{3+} \) (initial state \( 4d^{10}4f^{1} \)) and \( \text{Ce}^{4+} (4d^{10}4f^{0}) \). The method of calculation was a local many-body approach similar to that used previously to understand the \( q \)-dependence of \( d-d \) excitations in NiO and CoO [39]. Hartree-Fock (HF)-based radial wave functions were used in evaluating the expression for the dynamical structure factor, \( S(q, \omega) \) in eq. (2). Expanding the exponential term in terms of spherical harmonics yields

\[
e^{i \mathbf{q} \cdot \mathbf{r}} = \sum_{k=0}^{2k} \frac{1}{k!} (2k+1) j_k(qr) C_{m}^{(k)}(\theta_r, \phi_r) C_{m}^{(k)}(\theta_q, \phi_q),
\]

with \( k \)-th-order spherical Bessel function, \( j_k(qr) \), for the \( q \)-dependent radial component and the angular
dependence, \( C_m^{(k)} = \sqrt{(4\pi/2k+1) \times Y_{km}} \), averaging out since the samples are powder or polycrystalline. Inserting eq. (3) into eq. (2) yields

\[
S(q, \omega) = \sum_{f} \sum_{k=0}^{\infty} D_k |\langle f(r)|j_k(qr)|i(r)\rangle|^2 \delta(E_i - E_f + \hbar\omega)
\]

(4)

with the HF radial wave functions \( f(r), i(r) \), and coefficients, \( D_k \). As the \( f \) wave function is odd under inversion and the \( d \) wave function even, only transitions of odd parity and \( f - d = 1 \leq k \leq d + f = 5 \) contribute to the intensity (\( f \) and \( d \) being the orbital angular momentum quantum numbers for \( f \) and \( d \) orbitals). In eq. (4), then, only terms \( k = 1, 3 \) and \( 5 \) survive, with \( k = 1 \) being the dipole transition. These terms for \( Ce^{4+} \) and \( Ce^{3+} \) are displayed in fig. 2 as are the calculated \( S(q, \omega) \).

The strength of the different \( k \)-term contributions to \( S(q, \omega) \) is dependent on \( q \) as per eq. (4) \([25,38]\). Agreement is good between the calculations and data, but not exact. In general, one finds that the change from dipole \((k = 1)\) to octupole \((k = 3)\) or higher transitions in the calculation occurs at higher \( q \) values than in the experiment. This is related to the general finding that within a HF calculation, the radial wave functions are less extended than in real systems, which results in the calculated Slater integrals being too large. It is well established \([40,41]\) that the Slater integrals for a real system involving \( 4f \) orbitals and other core orbitals can be quite strongly reduced compared to those obtained from HF calculations. One reason for this is strong correlation effects between the electrons in spatially overlapping \( 4d \) and \( 4f \) wave functions and the very strong Coulomb and exchange interactions. The very large multiplet energy spread for the final states in configurations like \( 4d^24f^1 \) also can lead to a partial breakdown of the usefulness in describing the full multiplet structure in terms of a single set of Slater integrals. These issues can be studied with configuration interaction approaches well known in atomic physics \([42]\). It will be interesting to see if such approaches can at least partly resolve the difference in the \( q \)-dependent cross-over from a dipole to a multipole transition-dominated NIXS spectrum. This requires however a detailed and systematic study of numerous excited state configurations which could contribute and will be reported on in future work.

The dipole features above 120 eV do not agree well with experiment. The calculated spectra are sharper and show less structure for this regime. This problem has been realized before for the description of XAS \([43]\). The \( 4d \) core-hole/\( 4f \) valence Coulomb interaction results in an extensive multiplet structure where some states are pushed to quite high energy. These high-energy final states interact strongly with continuum states that are equal or lower in energy than the highest multiplets of the \( 4d^24f^{n+1} \) configuration. This interaction results in the characteristic shape of the observed higher multiplets (giant dipole resonance). For \( Ce^{4+} \) (or \( La^{3+} \)), which has a singlet \( S \) initial state, the final state due to a dipole \((k = 1)\)
Fig. 2: Calculated momentum-dependent multiplet structures for a) Ce\(^{4+}\)(4\(f^0\)) and b) Ce\(^{3+}\)(4\(f^1\)). The more intense components of the dipole terms in the calculated \(S(q,\omega)\) have been truncated for clarity. The individual multipole terms \(k = 1\) (dipole, dashed line), \(k = 3\) (solid line) and \(k = 5\) (dash-dotted line) contributing to the calculated \(S(q,\omega)\) at the \(N_{L5}\) edge are shown in the upper panel.

Fig. 3: The momentum \(q\) dependence of the contribution to \(S(q,\omega)\) from the \(4d\) initial state for a powder sample of CeO\(_2\).

excitation will have \(P\) character whereas an octupole excitation \((k = 3)\) will excite into states with \(F\) character. The state with \(P\) character is the highest multiplet of the \(4d^04f^1\) configuration. One can see in fig. 1 that the energy difference between these different multiplets is of the order of 15 eV.

The fact that the lower-energy, non-dipole resonances are not broadened by interaction with the continuum simplifies both their detection by NIXS and their explanation. While the preceding calculations have been specific to the case of Ce\(^{3+}/Ce^{4+}\), it is important to recognize that the physical issues involved are quite general. We anticipate that analogous multiplet-like features will be observed in any \(f\)-electron system, and that the issues of valence, hybridization, and final-state effects will each play a role in the resulting high-\(q\) NIXS spectra.

We have limited the present theoretical treatment to the ionic compounds but must still consider the influence of \(4f\) hybridization. Figure 3 contains the \(q\)-dependent NIXS data for CeO\(_2\). As with the phosphates, there is a change with increasing \(q\) from a giant dipole resonance to a multiplet structure at lower energy. Overall, the data for CeO\(_2\) resembles that for a \(4f^0\) system. The low-\(q\) giant resonance resembles that observed by XAS [9,10]. Near 4.6 \(\text{Å}^{-1}\), two peaks appear \(\sim 15\text{eV}\) below the giant resonance and additional features appear near 7.7 \(\text{Å}^{-1}\). However, compared to LaPO\(_4\), the features are
High multipole transitions in NIXS: Valence and hybridization in 4f systems

![Graph showing multiplet structures at high-q](image)

**Fig. 4**: A comparison of the high-q average multiplet structures at the N\textsubscript{4,5} region of the measured NIXS spectra for LaPO\textsubscript{4}, CeO\textsubscript{2}, CeRh\textsubscript{3}, and CePO\textsubscript{4} showing the influence of 4f hybridization on CeO\textsubscript{2} and CeRh\textsubscript{3}.

broadened. This is better illustrated in fig. 4, where the high-q data for LaPO\textsubscript{4}, CePO\textsubscript{4}, CeO\textsubscript{2} and CeRh\textsubscript{3} are compared directly. Multiplet features can be resolved in CeO\textsubscript{2}, but do appear broader than the (shifted) La compound. This suggests that the 4f states are largely unoccupied in CeO\textsubscript{2} but with some hybridization (between Ce 4f and O 2p states [15]). This is consistent with electronic-structure calculations [15], with oxygen K-edge data on CeO\textsubscript{2} and Ce\textsubscript{2}O\textsubscript{3} [16], where a pre-edge peak associated with 4f\textsuperscript{0} character is readily distinguished from a pre-edge feature associated with 4f\textsuperscript{1} interacting with O 2p states. Cerium 4f states in intermetallic CeRh\textsubscript{3} are considered to be more strongly hybridized than cerium in CeO\textsubscript{2} (becoming band-like [44]). This is observable in the NIXS N\textsubscript{4,5} region by the lack of resolvable features in a pre-threshold peak that has a maximum at an energy loss comparable to, and is asymmetric to lower energy loss more like the 4f\textsuperscript{0} materials than the 4f\textsuperscript{1} cerium phosphate. It is evident, then, that the manifestation of hybridization effects (covalency) in f-electron compounds is readily observable by broadening in pre-threshold multiplet features. It is in this area —covalence effects— that future theoretical treatments on N\textsubscript{4,5} NIXS must be directed in order to better understand 4f interactions in these materials.

Before concluding, it is interesting to consider the possible future application of N\textsubscript{4,5} NIXS to single crystals of f-electron materials. For single-crystal measurements, the angular dependence will remain in eq. (3) and S(q,\omega) will provide additional information about the local electronic properties. XAS and core shell NIXS measurements on single crystals of low-Z compounds show a strong sensitivity to anisotropy in the local electronic structure, such as those resulting from the details of chemical bonding [45–47]. The sensitivity of N\textsubscript{4,5} NIXS to such effects would provide a measure of the involvement of f-electrons in bonding. The evolution of the l- and m-dependent selection rules at high q also suggest possible sensitivity of N\textsubscript{4,5} NIXS to the ground-state symmetry, or orbital or magnetic ordering. Single-crystal effects in N\textsubscript{4,5} NIXS may be modeled by methods similar to those used recently [39] to treat NIXS from weakly bound electrons in single-crystal NiO and CoO [20].

In summary, we have examined a number of cerium-containing compounds near the Ce N\textsubscript{4,5} resonance using momentum-dependent non-resonant inelastic X-ray scattering. The spectra demonstrate a transition with increasing momentum transfer from dipole-like behavior similar to XAS measurements to growth of momentum-dependent multiplet features. The resulting multiplet features are valence and hybridization sensitive. Results for a 4f\textsuperscript{1} ionic compound, CePO\textsubscript{4}, are readily distinguishable from a 4f\textsuperscript{0} ionic compound, LaPO\textsubscript{4}, Hartree-Fock–based calculations are able to model the multiplet structures for the ionic compounds with good agreement of the q-dependence. Broadening of the multiplet features is signature behavior of interaction between the f-states and conduction or ligand states, as evidenced by the behavior of two classic 4f-interacting materials, CeO\textsubscript{2} and CeRh\textsubscript{3}. The ability to observe these q-dependent pre-threshold resonances outside the dipole limit is expected to be generic and thus provides a new spectroscopic tool for investigations of the physics and chemistry of f-electron systems.

***

This work was supported by the U.S. Department of Energy - Basic Energy Sciences, the Office of Naval Research, the Bosack and Kruger Foundation, the Natural Sciences and Engineering Research Council of Canada, the Canadian Institute for Advanced Research and the Deutsche Forschungsgemeinschaft. We would like to thank J. Garrett of BIMS, McMaster University for the CeRh\textsubscript{3} sample and K. Nagle of the University of Washington for answering numerous LERIX-related questions. PNC/XOR facilities at the Advanced Photon Source, and research at these facilities, are supported by the U.S. Department of Energy - Basic Energy Sciences, a major facilities access grant from NSERC, the University of Washington, Simon Fraser University and the Advanced Photon Source.

**REFERENCES**