

Probing Multiplet States in Cerium Compounds through q-Dependent X-ray Raman Measurements

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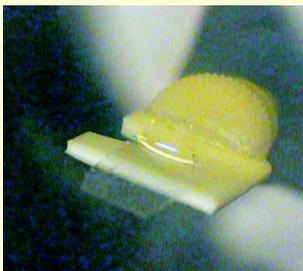


Abstract

We have used momentum-dependent X-ray Raman techniques available at the Sector 20 LERIX facility to study low-energy Cerium edges normally only accessible by soft x-ray, ultra-violet or electron techniques. Bulk cerium compounds CeO_2 , CePO_4 , CeF_3 , CeF_4 and CeRh_3 have yielded results indicating a very strong q-dependence to the edge resonances, particularly for the $N_{4,5}$ edges. At low momentum transfer, giant dipole resonances consistent with the $N_{4,5}$ edges measured by absorption (VUV, XAS) or electron-energy-loss (EELS) spectroscopies are observed. Measurements using LERIX indicate a complete transfer of oscillator strength to multiplet resonances at high-momentum transfer, with four readily distinguishable multiplet features present in the more-ionic compounds but less-resolved in the intermetallic compound. The relative strengths of these features are dependent on cerium valence but the energy-loss positions of the multiplets exhibit little dependence on valence or near-neighbour atom type.

Sample Preparation

Commercial powders (Alfa) of $\text{CeF}_3 \cdot n\text{H}_2\text{O}$, $\text{CeF}_4 \cdot n\text{H}_2\text{O}$, CePO_4 and CeO_2 were pressed into pellets approximately 0.25 mm thick and sectioned (broken) into pieces for mounting. The CeRh_3 sample was prepared from 99.9% pure elements (Alfa) by arc-melting and subsequent anneal under vacuum for 1 week at 800°C. The final mass of the arc-melted bead was within 1.5% of the stoichiometric value. The bead was cracked under liquid nitrogen to liberate a pale-metallic-pink rectangular fragment roughly $2.5 \times 1.5 \times 0.75 \text{ mm}^3$ from the interior of the bead. All samples were adhered to notched teflon holders with double-sided tape, as per the figure above, for mounting in the LERIX instrument.

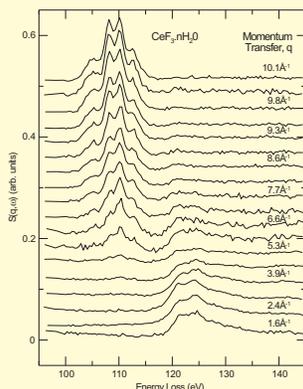


A section of CeF_3 pellet being measured in the LERIX apparatus at the PNC/XOR ID beamline, Sector 20 of the Advanced Photon Source, Argonne National Laboratory.

Introduction

Interactions between f-electrons and ligand or conduction states can strongly influence the physical and electronic behavior of rare-earth materials, particularly for cerium compounds, where the possibility of mixed-valence can arise. Numerous spectroscopic methods have been used to probe these interactions [1-5] with most limited to or dominated by dipole resonances. Multiplet structures observed by these methods provide considerable insight into 4f occupation and exchange interaction energies but surface and bulk contributions to these features when examining M, N or higher shells must both be considered due to the nature of the probes: electrons, soft x-rays or ultra-violet light.

X-ray Raman techniques [6-8], combined with high-brilliance synchrotrons, have opened up a new means of probing the electronic behavior of such systems by examining the momentum dependence of the edge resonances. Here we report the first observations of cerium multiplet structure at high momentum transfer obtained using the LERIX end-station at PNC/XOR.



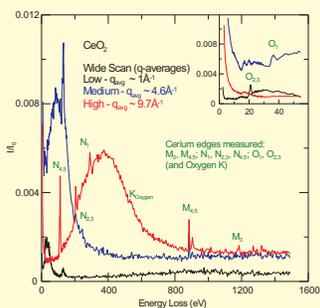
Results

ABOVE: Raw data for CeO_2 for low, medium and high momentum transfer. Multiple edges visible in the wide scan on top of the elastic (9893.3eV) and Compton background. Dipole-behavior occurs to the right of the Compton peak; non-dipole to the left. $N_{4,5}$ edges give the strongest response.

LEFT & RIGHT: Evolution of the $S(q, \omega)$ intensities as a function of momentum transfer and energy loss. Giant dipole resonances at low q diminish and multiplet resonances emerge with increasing q. Multiplet structure also exhibits q-dependence. Similar behavior has been observed in CEELS measurements [1] but without loss of the dipole resonance.

BELOW: Comparisons of the low-q and high-q averages of the five compounds studied.

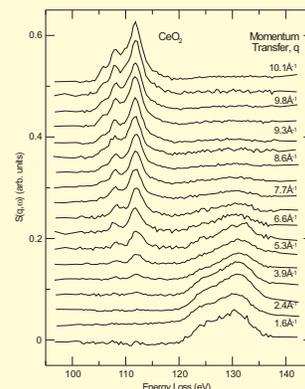
BOTTOM: Estimates of multiplet peak positions for CeF_3 and CeO_2 . Five features can be identified in both spectra. Monochromator resolution ($\sim 1.4\text{eV}$ at 10keV) is likely the limiting factor for resolving structures.



X-ray Measurements

Experiments were carried out at the Sector 20 insertion device beamline at the Advanced Photon Source, Argonne National Laboratory [9]. For these measurements, toroidal focusing of the monochromatic beam was performed, giving approximately 10^{13} photons/s incident on the samples. Samples were mounted and aligned within the LERIX instrument [10] with the full 19-detector array installed. Scattered intensities were normalised to a reference ion chamber upstream of the instrument.

The CeF_4 sample became discolored promptly when in the x-ray beam, indicating possible beam damage. Due to the heavier surrounding matrix in CeRh_3 , the scattered intensities were lower for the same integration times as the other samples.



Discussion

Low-q resonances agree with XAS and related measurements [1-5] of the Ce $N_{4,5}$ edges. CeF_4 broader to lower energy may be the result of beam damage - mixed 3+ and 4+ sample possible.

High-q multiplet structures show dependence on valence.

Trivalent CePO_4 and CeF_3 are very similar. Both CeF_4 and CeO_2 show pronounced feature at higher energy loss.

Multiplet structures appear over similar energy range as those observed by XAS and EELS [1-5], but dipole resonance suppressed.

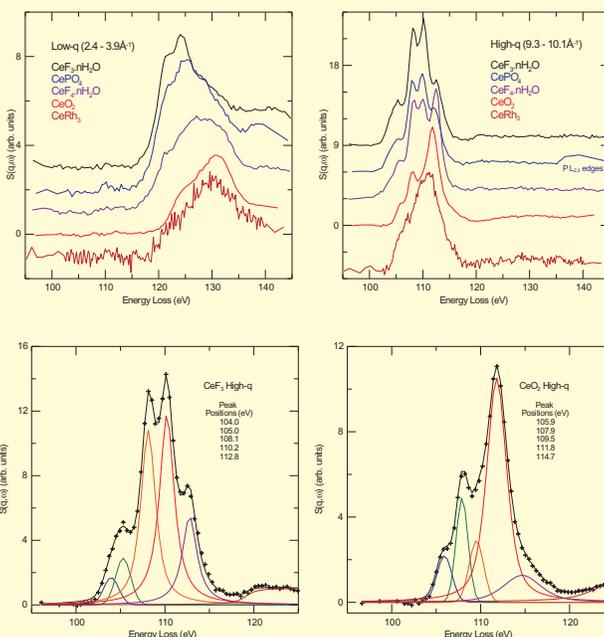
CeRh_3 exhibits strong, but not well-resolved peak structure in q-dependent Raman. Qualitatively similar, albeit broadened, structure when compared to CeO_2 . This is *in contrast* to XAS and photoemission measurements.

What are the origins of the multiplets in q-dependent Raman?

NEW theoretical treatment needed!!!

LERIX THEORY PRIZE:

A bottle to the theory group that first quantitatively explains the q-dependent multiplet structures!



Acknowledgements

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