Local Electronic and Atomic Structure of Ce^{3+} -Containing Fluoride/Oxide Determined by TEM-EELS and First-Principles Calculations

Ikuo Nishida, Kazuyoshi Tatsumi and Shunsuke Muto

Department of Materials, Physics and Energy Engineering, Nagoya University, Nagoya 456-8587, Japan

We investigated the local atomic and electronic structure around Ce in CeF_3 and Ce_2O_3 by the combination analysis of F- and O-K shell electron energy loss near edge structures (ELNES) and first-principles calculations. The energy width of the main edge structure depended on the interaction between Ce5d orbitals and the neighboring F/O atoms. Not only ELNES but also the reported emission and excitation spectra were qualitatively consistent with the electronic structures of density functional theory (DFT) calculations with Hubbard U for the Ce4f energy correction. Main factors determining the emission wavelength of the fluoride and Ce-doped oxides were discussed.

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1. Introduction

Ce^{3+} in solid-state materials exhibit various functional properties. For example, CeF_3 and Ce^{3+} -doped oxides, such as $\text{Y}_3\text{Al}_5\text{O}_{12}$ garnet (YAG), are utilized for scintillating and/or white light generating applications because of their characteristic emission properties.¹⁻⁵⁾ $\text{Ce}_2\text{Zr}_2\text{O}_{7-8}$ ordered phases, which have efficient oxygen desorption/absorption properties, are used as catalytic promoters for reactions cleaning automotive exhaust gases.⁶⁾ These materials properties are closely related to the configurations of Ce4f-based states. Ce5d-based states are also important for photoemission because the emission is due to electron transition from the lowest excited Ce^{3+} 5d level to the ground 4f level.¹⁾

Among the spectroscopic methods to probe these electronic structures, the Ce- $M_{4,5}$ near edge structures of electron energy loss and x-ray absorption spectra (ELNES and XANES) have been known to change the intensity ratio of M_5 to M_4 peaks according to the formal valency of Ce.⁷⁾ Recently, in addition to Ce- $M_{4,5}$ XAS, Ce 4f to 3d resonant X-ray fluorescence (RXF) spectra have been used to investigate the Ce valence in fluorides and oxides, combined with theoretical calculations based on Anderson's impurity model.^{8,9)} Although photoluminescence stimulated excitation spectra in the ultraviolet and visible light range (UV-VIS) provide information on unoccupied Ce5d states, their spectral structures have not been compared with first-principles calculations. As an alternative spectroscopic route, anion K-edge ELNES/XANES, which reflect unoccupied anion p-like states, can be interpreted by first-principles electronic structure calculations with relative success. Because the conduction bands are mainly composed of cationic orbitals, the spectral structures indirectly convey information on the Ce5d states.

The present study investigates the electronic structure around Ce^{3+} by a combination of anion-K ELNES and first-principles calculations. A comparison between the typical Ce^{3+} -containing materials CeF_3 and Ce_2O_3 will exemplify the relationship between the local structures around Ce^{3+} and the emission properties of the materials.

2. Methods

2.1 TEM-EELS measurement

A commercially available CeF_3 powder was used for EELS. The powder x-ray diffraction pattern was most consistent with the reported profile of CeF_3 .¹⁰⁾ The sample was dispersed in ethanol and scooped onto a holey carbon microgrid supported by a copper mesh. Spectra were acquired with a Gatan Enfina 1000 EELS spectrometer attached to a Jeol JEM-200CX operated at an accelerating voltage of 160 keV with a LaB₆ electron source. The energy resolution at the zero loss peak was 0.7 eV and the energy dispersion was 0.2 eV/channel. In order to prevent electron irradiation damage on the sample, we measured F-K ELNES using an acquisition time of 1 s. We measured 12 spectra at different sample areas. The spectra contained a significant level of noise, which was reduced by Pixon based deconvolution.^{11,12)} In this process, the corresponding low loss spectra were used as a Point-Response Function (PRF). The restored spectra were summed with the main peak position aligned at the same energy so as to reduce the remaining statistical noise. The absence of O-K ELNES confirmed that there was no significant oxidation on the measured areas. Our EELS measurement on Ce_2O_3 was unsuccessful because of the rapid oxidation of the sample during its transfer into the TEM.

2.2 Theoretical calculations

In order to theoretically calculate F- and O-K spectra including their fine peak structures, we adopted a first-principles full-potential augmented plane waves plus local orbital (APW + lo) method (WIEN2k¹³⁾) within the framework of the general gradient approximation (GGA)¹⁴⁾ and GGA + U approach.^{15,16)} In GGA + U , Coulomb interactions among the localized electrons are corrected by the Hubbard U parameter.¹⁵⁾ Its applications to ceria have been reported by several authors.^{17,18)} However, the choice of U is ambiguous, and it is not trivial to determine its value *a priori*, though there are attempts to extract it from standard first-principles calculations. We selected $U = 5.0$ and 2.5 eV for

CeF₃ and Ce₂O₃, respectively. These were the values that reproduced the experimental spectral features most accurately. The value for Ce₂O₃ was reported to provide reasonable agreement with experimental lattice constants and formation energies.¹⁸⁾

As is well established, it is essential to take into account the core-hole effect in order to reproduce the spectral fine structures of ELNES.¹⁹⁾ We used supercells containing one excited atom with a hole at the 1s state. The supercell for CeF₃ was set to extend the cell vectors, $\mathbf{a}_{\text{super}}$, $\mathbf{b}_{\text{super}}$ and $\mathbf{c}_{\text{super}}$ as $\mathbf{a}_{\text{super}} = \mathbf{a} - \mathbf{b}$, $\mathbf{b}_{\text{super}} = \mathbf{a} + \mathbf{b} - \mathbf{c}$ and $\mathbf{c}_{\text{super}} = \mathbf{a} + \mathbf{b} + \mathbf{c}$, where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are the primitive cell vectors. The supercell vectors for the Ce₂O₃ calculation were set to be $\mathbf{a}_{\text{super}} = 3\mathbf{a}$, $\mathbf{b}_{\text{super}} = 3\mathbf{b}$ and $\mathbf{c}_{\text{super}} = 2\mathbf{c}$. These CeF₃ and Ce₂O₃ supercells contain 96 and 90 atoms, respectively, with a core hole separated by more than 10 Å from the core-holed atoms in the adjacent cells. The transition energy of the inner shell spectra was evaluated by the total energy difference between the core-holed supercell and non-core-holed supercell. The details of the APW + lo calculations are as follows: the Muffin-tin radius (R_{MT}) of each atom was chosen to be as large as possible in the cell, and $R_{\text{MT}}K_{\text{MAX}}$, which corresponds to the plane wave cutoff, was set by using the product of the smallest R_{MT} and K_{max} (3.0 Ry^{1/2}). The Monkhorst-Pack scheme²⁰⁾ was employed on a $2 \times 2 \times 2$ mesh for $\mathbf{k}$ -point sampling in the reciprocal cell. The transition probabilities were calculated within the electric dipole approximation. Final spectra were broadened by a Gaussian function with a FWHM of 1.0 eV.

In order to discuss the underlying difference between the spectra of CeF₃ and Ce₂O₃ in terms of atomic orbital interactions, we adopted a first-principles molecular orbital (MO) method²¹⁾ based on the density functional theory (DFT) in the local density approximation. In the MO calculations, we adopted the Slater's transition state method, where 0.5 holes are introduced at the excitation shell and the transition energy is approximated by the energy differences between the eigenvalues of the core orbital with 0.5 holes and the unoccupied molecular orbitals. For a simple interpretation of the orbital interactions, a minimal atomic basis set, Ce[1s2sp3spd4spdf5spd], F[1s2sp] and O[1s2sp], was adopted. Cluster models for the MO calculations contained approximately 90 atoms. The transition probabilities and final spectra were obtained in the same manner as in the APW + lo calculations. Partial density of states (PDOS) and overlap population diagrams (OPD)²²⁾ were calculated using the same Gaussian broadening as the broadening for the theoretical ELNES. Since relativistic calculations including spin-orbit coupling merely affected the theoretical anion-K ELNES, we neglected its effects in our calculations.

2.3 Crystal structures and their theoretical optimization

CeF₃ and Ce₂O₃ have trigonal symmetry of the space groups $P\bar{3}c1$ and $P\bar{3}m1$, respectively. Prior to the spectral calculations, all crystal parameters were optimized within GGA and GGA + U band calculations. The projected augmented-wave method²³⁾ was employed to reduce computational cost. The cutoff energy of the plane wave basis was 500 eV and $4 \times 4 \times 3$ and $7 \times 7 \times 4$ meshes were employed for $\mathbf{k}$ -point sampling in the reciprocal cells of CeF₃ and

Table 1 Comparison of the crystal parameters between the present calculation and the reported experimental values.

CeF ₃	GGA	GGA + U	Expt. ²⁴⁾	Difference	
a (Å)	7.20	7.22	7.1412	0.06	0.08
c (Å)	7.29	7.40	7.2989	0.00	0.10
Ce 6f x	0.333	0.333	0.3406	-0.007	-0.007
F _{site2} 4d z	0.250	0.249	0.3186	-0.068	-0.070
F _{site3} 12g x	0.333	0.331	0.3264	0.006	0.005
y	-0.000	-0.003	-0.058	0.058	0.055
z	0.578	0.580	0.5796	-0.002	0.000
Ce ₂ O ₃	GGA	GGA + U	Expt. ²⁵⁾	Difference	
a (Å)	3.82	3.90	3.891	-0.07	0.00
c (Å)	6.08	6.15	6.059	0.02	0.09
Ce 2d z	0.246	0.247	0.24543	0.001	0.002
O _{site2} 2d z	0.641	0.644	0.6471	-0.006	-0.003

Ce₂O₃, respectively. The optimized lattice parameters are shown in Table 1. The lattice constants are consistent with experimentally reported values to within ~1%, which is a typical GGA-based calculation accuracy. Internal parameters specific to the space groups of CeF₃ and Ce₂O₃ are also presented in Table 1. For Ce₂O₃, the theoretical values reproduced the experimental values fairly well. However, in the case of the two fluorine parameters, z and y of Wyckoff's notation 4d and 12g for CeF₃, there was significant discrepancy between the theoretical and experimental values. The reason for this is still unclear. We calculated F-K ELNES using both of the crystal parameters. The relative intensities of the fine structures in the spectra differed from each other, though the main features of interest were obtained similarly by the two structures. For simplicity, we will hereafter show the results obtained using the theoretically optimized crystal parameters.

The crystal structures of CeF₃ and Ce₂O₃ are illustrated in Fig. 1. The trigonal cell of CeF₃ contains one Ce site surrounded by 11 F atoms. F occupies two 3-coordinated 2a and 4d sites (F_{2a} and F_{4d}), and one 4-coordinated 12g site (F_{12g}). F_{2a} and F_{4d} are almost on the same *ab* planes. In the experimental crystal structure, F_{4d} is displaced along the *c* axis and F_{12g} is displaced parallel to the *ab* planes, according to the internal parameters z and y. In Ce₂O₃, Ce occupies a 7-coordinated 2d site and O occupies 4-coordinated 1a and 6-coordinated 2d sites (O_{1a} and O_{2d}).

3. Results and Discussion

3.1 Anion K-shell ELNES of CeF₃ and Ce₂O₃

Figure 2 shows the experimental and theoretical F- and O-K ELNES. In the experimental spectra, the energy widths of their main structures, including the large peak A and its shoulder B for F-K and three broad peaks A, B and C for O-K, exhibit distinct differences. The energy widths are 4.5 and 8.3 eV, respectively, for the F- and O-K spectra, which were evaluated from the peak distance between the maxima of the second differentiated spectra that appeared in the lowest and highest ends of the main structures.

The GGA + U scheme reproduced the experimental peak profiles well, while the GGA without U presented an extra

Fig. 1 Crystal structures of CeF_3 and Ce_2O_3 . Cerium coordination is shown in (a) and (c) for theoretically optimized structures of CeF_3 and Ce_2O_3 . Unit cells are shown in (b), (b') and (d) for the theoretically optimized and experimental structures of CeF_3 and theoretically optimized structure of Ce_2O_3 . Anions occupying different sites are differently colored.

Fig. 2 Experimental and theoretical F- and O-K ELNES. Main structure width is evaluated as the distance between the positions of the broken lines corresponding to the minimum and maximum in the second derivative spectra.

peak at the lower energy side. Because the Hubbard U incorporated into the Ce $4f$ orbitals corrects the Coulomb repulsion of Ce $4f$ electrons at each site within the one-electron approximation, the extra peak is due to underestimation of the Ce $4f$ states energies. Since the other fine structures are quite similar irrespective of U incorporation, the chemical bonding behind the experimental spectral profiles can be roughly interpreted on the basis of calculations without the Hubbard U . Although the MO calculations reproduced the peak profiles less accurately than the GGA and GGA + U band methods, the main structures in the F- and O-K spectra quantitatively reproduced the energy

widths of 3.4 and 6.2 eV, respectively, in agreement with the experimental trends.

3.2 Atomic orbital interactions in the unoccupied states of CeF_3 and Ce_2O_3

The main peaks of the F-K spectrum in CeF_3 are much narrower than those of O-K in Ce_2O_3 . This trend is seen in both the experimental and theoretical spectra. In order to reveal the difference in terms of chemical bonding, the unoccupied PDOS of CeF_3 and Ce_2O_3 are shown in Figs. 3(a) and 3(b), and the OPD between Ce and its neighboring F and O in (c) and (d), respectively, for the

Fig. 3 Partial densities of states and overlap population diagrams around Ce atoms, calculated by the molecular orbital method. The labels A_1 , B_1 , C_1 are identical to those in Fig. 4.

non-core-holed, ground state electronic structures of the MO calculations. The Fermi level is set to zero in each figure. The main peak structures of the ELNES correspond to the Ce5d-derived states, which range from 5 to 9 eV above the Fermi level for CeF₃ and from 3 to 9 eV for Ce₂O₃, as shown in Figs. 3(a) and 3(b). Since the intensities of those OPD are negative, the corresponding interactions between the Ce and anion atoms are all antibonding in nature. In CeF₃ (Fig. 3(c)), the low- (~6 eV) and high-energy (~8 eV) states show similar negative OPD intensities. In Ce₂O₃ (Fig. 3(d)), the low-energy (~4 eV) states show much weaker negative OPD intensities than the high-energy (~8 eV) states. Larger OP intensities correspond to larger spatial overlaps between the two molecular orbitals, which in turn promote higher antibonding energy levels.²⁷⁾ The spatial overlaps between the Ce5d and the anion orbitals show a wider variation in the Ce5d-derived states in Ce₂O₃ than in CeF₃, which results in the larger energy width of Ce5d PDOS and the main peak structures in the ELNES.

3.3 Orientation of Ce5d orbitals with respect to the nearest neighbor anions

Let us examine the energy width differences in Ce5d-derived states in an alternative way, namely, by visualizing the orientation relations of Ce 5d orbitals with respect to the nearest neighbor anions, which allows us to obtain an intuitive understanding of the features. Figure 4 shows the wavefunction isosurfaces of the representative Ce5d-derived states in the MO calculations, whose energy levels are indicated in Fig. 3. The isosurfaces are shown up to a distance of 1.85 Å from the Ce site so as to reveal the relative orientation of the Ce5d orbital with respect to the nearest neighbor anions. In CeF₃, one of the four radial principal axes of the A_1 state orbital points approximately towards the F6 atom, while none of the other three axes indicate any of the other 10 nearest neighbor anions. Three of the four B_1 state orbital principal axes extend, respectively, towards F1, F2 and F8, while the last one does not point to any of the other 8 anions.

In Ce₂O₃, the main principal axis of the Ce5d orbital at the low-energy state A_1 points toward none of the nearest O atoms, but lies on the O1-O3-O2-O5-O1 plane with the toroidal mother line parallel to the O1-O3 and O2-O5 ridgelines. On the other hand, the convex directions of the high-energy state C_1 orbital point approximately to the six nearest O atoms except O7.

The above-mentioned features again suggest that the spatial overlaps between Ce5d and the nearest neighbor anion orbitals are much smaller (larger) at the lower (higher) energy A_1 (C_1) states in Ce₂O₃. Thus, the large variation of the spatial overlaps results in the larger energy width of Ce5d-derived states in Ce₂O₃.

The Ce5d orbitals of A_1 and C_1 in Ce₂O₃ show shapes very similar to the t_{2g} and e_g d atomic orbitals, respectively, under the O_h symmetry field. By contrast, the Ce in fluoride is coordinated by many more anions whose relative positions are incompatible with the principal axis directions of the Ce5d orbitals, and whose shape looks more like d orbitals under the spherical symmetry field. Thus, we can say that the O_h -like crystal field gives rise to a larger splitting of the Ce5d states in Ce₂O₃ than the sphere-like crystal field in CeF₃.

3.4 Energy gap between Ce5d-4f states and related physical properties

CeF₃ is used in scintillators because of its ultraviolet fluorescence with a short decay time.¹⁻³⁾ Ce³⁺-doped oxides such as YAG have not only been studied for scintillator applications because of their yellow fluorescence,⁴⁾ but also because their phosphorescence properties are believed to make them promising candidates for white light emission devices, coupled with highly efficient light emitting diodes (LED).⁵⁾ The light emissions of fluoride and oxides are due to the transition from the lowest excited Ce³⁺ 5d level to the ground 4f level. In calculations within the one-electron approximation with the Hubbard U correction for 4f electrons, the relative energy difference between the local-

Fig. 4 Isosurface plots of wavefunctions around Ce for the energy levels A_1 , B_1 , C_1 in Fig. 3. Atoms are colored in the same manner as in Fig. 1. O7 is identical to the oxygen atom bonded to Ce with a bond length of 2.43 Å in Fig. 1.

Fig. 5 Partial densities of states around the Ce4f-5d gap, calculated by the GGA + U band method.

ized Ce 4f level and the bottom of the unoccupied Ce 5d states would roughly correspond to the emission energy.

Figure 5 shows the density of states near the 4f-5d gap, calculated with the GGA + U scheme. The fluoride shows a much larger 4f-5d gap than the oxide, which is qualitatively consistent with the experimental emission energies (CeF₃: 4.4 eV;² Ce-doped YAG: 2.4 eV⁴). It should be noted that the theoretical band gap between the unoccupied Ce5d and valence bands would be systematically smaller than the experimental values. This is a well known deficiency of DFT.

Indeed, our theoretical value for CeF₃ is 7 eV, which is smaller than the experimental ~ 10 eV.¹⁾

In the theoretical DOS, the 4f-5d gap energy is thought to mainly depend on two factors. One is the energy width of the Ce5d states due to the crystal field splitting. The other is Hubbard U , which splits the occupied and unoccupied Ce4f states in theoretical DOS. The former presumably depends on the local environment around Ce, as discussed in the previous sections. Experimental UV-VIS excitation spectra provided information on the unoccupied

Fig. 6 Schematics of the one-electron energy levels of CeF_3 and Ce_2O_3 . The multi-electron energy levels related to the photoemission process are inserted between the one-electron schemes. The electronic transitions associated with the emission are also shown by black (excitation transitions), and gray (non-radiative transitions) and white (emission transitions) arrows.

$\text{Ce}5d$ states; the energy widths of $\text{Ce}5d$ for CeF_3 and Ce -doped YAG are estimated to be 2.3²⁾ and 6.9⁴⁾ eV, respectively, which are consistent with the widths of the $\text{Ce}5d$ DOS in Figs. 5(a) and 5(b). Concerning the latter factor, when we compared the calculation results for the same compound with $U = 5.0$ and 2.5 eV, the $\text{Ce}4f$ energy position was shifted by 1.2 eV, approximately half the difference in the U values. On the other hand, the different U value merely shifted the $\text{Ce}5d$ position with respect to the valence bands.

The effects of these two factors, Hubbard U and $\text{Ce}5d$ energy width, on the light emission properties are schematized in Fig. 6. In the one-electron energy level diagrams, the conduction bands, mainly composed of the $\text{Ce}5d$, and the valence bands, mainly composed of the anion $2p$, are represented by rectangles with energy widths reflecting the GGA + U calculation results. The unoccupied $\text{Ce}4f$ DOS is also schematized so as to express the $\text{Ce}4f$ split by the Hubbard U . The energy levels of the photoemission-related configurations, $\text{Ce}4f^1$ and $\text{Ce}4f^0 5d^1$, are inserted for better understanding. The luminescent photon energy corresponds to the energy between the $\text{Ce}4f^1$ level and the bottom of the $\text{Ce}4f^0 5d^1$ levels. The unoccupied $\text{Ce}4f$ states in the one-electron energy level diagrams could correspond to the $\text{Ce}4f^2 + \text{Ce}4f^0$ configuration, which can be neglected for the photon emission, because the transition probabilities between $\text{Ce}4f^2 + \text{Ce}4f^0$ and $\text{Ce}4f^1$ (or $\text{Ce}4f^0 5d^1$) would be much lower than those between $\text{Ce}4f^1$ and $\text{Ce}4f^0 5d^1$. Since the $\text{Ce}5d$ energy width, rather than U , depends more strongly on the local environment around Ce^{3+} , a modification of the local atomic arrangement, e.g., by co-doping other cations, could tune the emission photon energy suitable for specific optical applications by changing the $\text{Ce}5d$ bandwidth.

4. Summary

We have investigated the local electronic structure around Ce^{3+} by comparing the experimental EELS and theoretical first-principles electronic structure of two typical Ce^{3+} -containing materials: CeF_3 and Ce_2O_3 . The main results can be summarized as follows:

- (1) F- and O-K ELNES including their fine structures were mostly reproduced by GGA + U calculations. The calculations without Hubbard U resulted in an extra peak on the lower energy side of the edge threshold. This was ascribed to incorrect evaluation of the Coulomb interaction between $\text{Ce} 4f$ electrons.
- (2) Except for the extra peak described above, all the calculations and experimental results showed a common trend: the energy width of the main spectral structure was much broader in O-K of Ce_2O_3 than in F-K of CeF_3 . This is due to the $\text{Ce}5d$ orientations with respect to the nearest neighbor anions. In Ce_2O_3 , the geometry of the nearest neighbor O atoms is compatible with the symmetry of the $\text{Ce}5d$ orbital, resulting in a much larger crystal field splitting of the $\text{Ce}5d$ -derived states.
- (3) The calculated $\text{Ce}5d$ energy widths and energy gaps between the occupied $\text{Ce} 4f$ level and the bottom of the unoccupied $\text{Ce} 5d$ states for the fluoride and oxide were qualitatively consistent with the reported experimental UV-VIS spectra. The $\text{Ce}5d$ energy width could be tuned for specific optical applications, for example, by doping the host crystal with different cations.

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