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$4f^{n-1}5d$ centroid shift in lanthanides and relation with anion polarizability, covalency, and cation electronegativity

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Abstract

Data collected on the centroid shift of the 5*d*-configuration of Ce^{3+} in oxide and fluoride compounds were recently analyzed with a model involving the correlated motion between 5*d*-electron and ligand electrons. The correlation effects are proportional to the polarizability of the anion ligands and it leads, like covalency, to lowering of the 5*d*-orbital energies. By means of ab initio Hartree–Fock-LCAO calculations including configuration interaction the contribution from covalency and correlated motion to the centroid shift are determined separately for Ce^{3+} in various compounds. It will be shown that in fluoride compounds, covalency provides an insignificant contribution. In oxides, polarizability appears to be of comparable importance as covalency.

Keywords: Centroid shift; Nephelauxetic effect; Lanthanides; Polarizability; Electronegativity; Covalency; Ce^{3+}; Spectroscopy; Configuration interaction; Correlated motion

1. Introduction

According to the definition by Jörgensen [1], the nephelauxetic effect is that the "phenomenological parameters of interelectron repulsion are smaller in complexes than in the corresponding gaseous ions." It leads to a displacement of levels to lower energy depending on the type of compound. The effect has been studied for the *ff*-transitions in lanthanides [2,3], the *dd*-transitions in transition metal elements [1], and the *sp*-transitions in Tl^+, Pb^{2+}, and Bi^{3+} [4,5]. The size of the effect can be characterized by the nephelauxetic ratio β as

$$1-\beta = hk, \tag{1}$$

where $1-\beta$ is written as a product of two functions, each of one variable [1]. h characterizes the anion ligands and k the metal. When anions or ionic complexes are put in the order of increasing h-parameter the well-known nephelauxetic series are obtained, i.e.,

$$\text{no ligands} \quad < F^- < H_2O < NH_3 < Cl^- < Br^- < N^{3-} < I^- < O^{2-} < S^{2-} < Se^{2-} \tag{2}$$

and

$$H_2O < SO_4^{2-} < CO_3^{2-} < PO_4^{3-} < BO_3^{3-} < SiO_4^{4-} < AlO_4^{5-} < O^{2-}. \tag{3}$$

The reduction of interelectron repulsion and the increase of h-parameter is often ascribed to the covalence [1,3], i.e., the sharing of electrons between the metal and the surrounding ligands. Although the term "nephelauxetic effect" literally means "charge cloud expansion", it is commonly used in a wider sense incorporating the effects of covalency also.

The ideas developed for the nephelauxetic effect in the above metal elements may also be used to describe the energy difference between the $4f^n$ and $4f^{n-1}5d$ configurations in lanthanides. There is however an essential difference. The lanthanides have only one single electron in the excited 5*d*-shell and interelectron repulsion between *d*-electrons is absent. Nevertheless, the 5*d*-configuration of Ce^{3+} is known to lower in energy by 5000–25 000 cm^{-1} depending on the type of compound [6–9]. The decrease relative to the free ion situation is known as the centroid shift ε_c [6]. Even in fluoride compounds where covalency between Ce^{3+} and fluorine ligands is very small, ε_c is still 5000–8000 cm^{-1} [6].

Covalency contributions to ε_c can be accounted for by means of single-particle theory like Hartree–Fock (HF)

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and density functional theory (DFT) [10]. For the fluoride compounds, Morrison suggested a contribution from two-electron interactions [11], i.e., one where the 5*d*-electron polarizes the ligand electrons that in turn interact back on the 5*d*-electron thus lowering its energy. In fact it describes a correlated motion between the 5*d*-electron and the ligand electrons. One may write

$$\varepsilon_c = \varepsilon_1 + \varepsilon_2 \tag{4}$$

to separate the contributions from single electron and the specific two-electron interaction.

The two-electron contribution ε_2 can be calculated classically [6,11],

$$\varepsilon_2 = \frac{e^2}{4\pi\varepsilon_0}(\langle r^2\rangle_{5d} - \langle r^2\rangle_{4f})\alpha \sum_{i=1}^{N} R_i^{-6} \equiv \sigma S, \tag{5}$$

where r represents the position of the electron in either the 5*d*- or 4*f*-orbital, and $\langle r^2\rangle$ is the expectation value of r^2. α is the polarizability of the anion ligands located at a distance R_i from Ce^{3+}. With $\sigma \equiv \langle r^2\rangle_{5d} - \langle r^2\rangle_{4f}$ and $S \equiv (e^2/4\pi\varepsilon_0)\alpha\sum_{i=1}^{N} R_i^{-6}$, Eq. (5) is like Eq. (1) written as a product of two functions. S characterizes the ligands and σ the lanthanide.

Defining the spectroscopic polarizability as

$$\alpha_{sp} \equiv \alpha\left(1 + \frac{\varepsilon_1}{\varepsilon_2}\right), \tag{6}$$

α_{sp} can be calculated from the observed centroid shift by substitution of ε_c and α_{sp} for ε_2 and α in Eq. (5), respectively. With this definition, α_{sp} is calculated as if it arose entirely from polarization effects. This is certainly not true and therefore α_{sp} should be regarded as a phenomenological parameter. Only when the ratio $\varepsilon_1/\varepsilon_2$ appears constant, α_{sp} will be proportional to the real polarizability.

A systematic study [6–9] in the literature on *fd*-excitation and absorption spectra on Ce^{3+} in compounds has provided values for the 5*d* centroid shift and from that values for α_{sp}. In this work, the relation between the centroid shift and physical and chemical properties of the compounds will be investigated. With a semi-empirical approach, a linear relationship between α_{sp} and the inverse square of the average cation electronegativity will be demonstrated to exist. The correlated motion has been implemented in ab initio calculations by extending the basic HF-LCAO approach with configuration interaction (CI) and using basis sets optimized for polarization on the anions [12]. Assumed that the CI mainly involves the correlated motion mentioned above it provides a means to separately determine the contributions from ε_1 and ε_2 to the centroid shift.

2. Results and discussion

Data on the centroid shift of Ce^{3+} in fluoride and oxide compounds was presented already in Refs. [6–9]. The values for α_{sp} calculated by using Eq. (5) can be found in Ref. [13]. Polarizability in the fluorides is around 1×10^{-30} m^3, see Fig. 1. The data on the oxide compounds are grouped following the same sequence as in Eq. (3). The oxygen polarizability is smallest in compounds with H_2O coordination around Ce^{3+}. α_{sp} tends to increase in the same sequence as the nephelauxetic series.

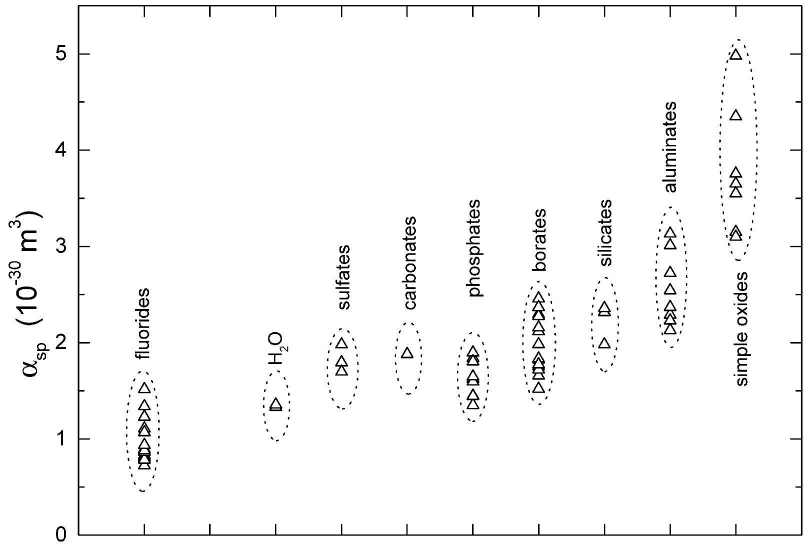

Fig. 1. The spectroscopic polarizability α_{sp} for the anions in fluoride and oxide compounds as calculated from the centroid shift of the 5*d*-configuration of Ce^{3+}.

In Ref. [13], a weighted average electronegativity χ_{av} of the cations in a compound was defined as

$$\chi_{av} \equiv \frac{1}{N_a} \sum_{i}^{N_c} \frac{z_i \chi_i}{\gamma}, \tag{7}$$

where the summation is over all cations N_c in the formula of the compound, and N_a is the number of anions in the formula. χ_i represents the electronegativity of cation i with formal charge z_i, and γ is the formal negative charge of the anion.

Fig. 2 shows the same data as in Fig. 1 but now displayed against χ_{av}^{-2}. The data on the oxides and the fluorides show a remarkably linear relation with χ_{av}^{-2}. The origin of this relation must be sought in the binding force constant of the ligand electrons [13,14]. Highly electronegative cations tend to bind anion ligands strongly. Both, the ligand polarizability and the covalency between ligand and Ce^{3+} will be reduced leading to small values for α_{sp} and ε_c. With this semi-empirically found relationship [13], it is possible to estimate the size of the centroid shift of the 5*d*-configuration of Ce^{3+} from information on the crystal structure and the type of cations in the compound.

Ab initio calculations by means of single-particle HF-LCAO fail to correctly reproduce the centroid shift. For example, Marsman et al. [10] calculate for $BaLiF_3 : Ce^{3+}$ an insignificant centroid shift of 170 cm^{-1} whereas experimentally 6540 cm^{-1} is observed, see Table 1. It is clear that the neglect of correlated motion is responsible for this large discrepancy. Recently, we have repaired this shortcoming by extending the HF-LCAO with CI [12]. By optimizing the basis set for the polarization of the anions, the correlated motion between 5*d*-electron and ligand electrons can be accounted for. By first performing HF-LCAO (using the optimized basis set) without multiparticle interaction and next with multiparticle interaction, the contributions from single electron (ε_1) and multielectron interactions (ε_2) can be determined separately. Results are compiled in Table 1.

In the calculations, a 5*d*-orbital needs to be occupied by an electron and next the energy is minimized by the HF-LCAO method. Severe computational problems may arise for the higher lying 5*d*-levels that are located well inside the conduction band (CB). The HF-LCAO code does not generate always the energy of the high-lying 5*d*-orbitals, but instead the electron falls down to the lowest 5*d*-orbital or to CB-levels followed by energy minimization. So far, we only managed to avoid this problem for lattices providing high point symmetry at both the Ce^{3+} and the anion site. Relaxation of the higher 5*d*-electrons to the lowest 5*d*-orbital is then symmetry restricted. Another problem influencing the stability is the size of the cluster containing the Ce^{3+} ion

Table 1
Calculated values for ε_1 and ε_2 (cm^{-1}) together with values on ε_c (cm^{-1}) and α_{sp} (10^{-30} m^3) from Ref. [13]

Comp.	ε_1	ε_2	ε_c	α_{sp}
$LiYF_4$	—	3790	5520	0.80
$BaLiF_3$	170	—	6540	1.34
BaF_2	320	3710	6470	1.52
$Y_3Al_5O_{12}$	2820	5330	14 700	2.72
$LaAlO_3$	3060	5170	≈14 800	3.01
CaO	6450	4850	≈20 500	5.0
$LaCl_3$	6210	7340	13 000	6.48
$LaBr_3$	6210	6230	15 900	11.1

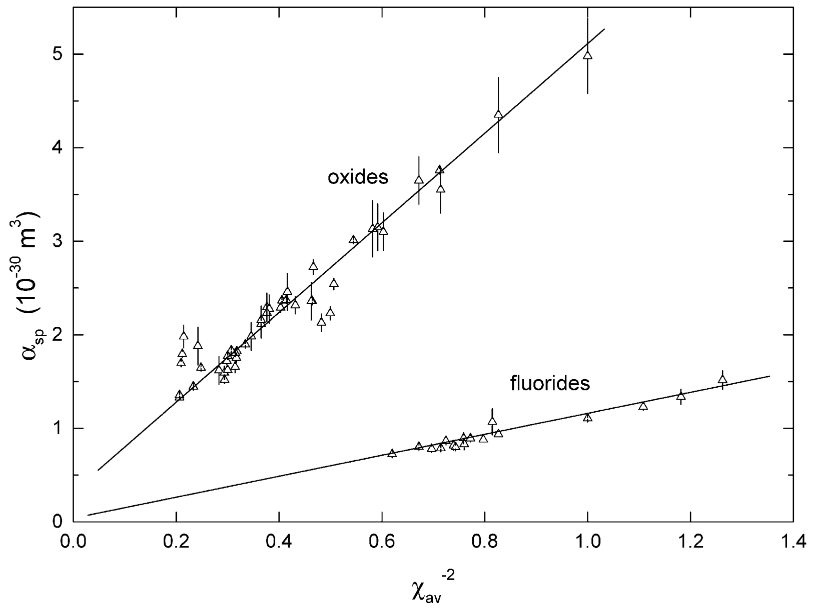

Fig. 2. Spectroscopic polarizability against the inverse square of the average cation electronegativity.

in the center. Besides the nearest coordinating anions it has been found essential to include all the cations that are coordinating these anions. However, even with these extended clusters of atoms, edge effects are still likely to be present. The size and importance of the edge effect is still a subject of further study.

Using the optimized basis sets, the energies of the five 5*d*-levels were calculated for Ce^{3+} in BaF_2, $Y_3Al_5O_{12}$, $LaAlO_3$, CaO, $LaCl_3$, and $LaBr_3$. The total crystal field splitting of the 5*d*-levels was reproduced within 5%. The average energy of the five 5*d*-levels provide the values for ε_1 in Table 1 which should be regarded as the contributions from covalency to the centroid shift. The same calculations performed including CI provides similar crystal field splitting but larger centroid shift. Although a clear separation between single- and multi-particle interaction cannot be made in CI, we assumed that ε_1 with CI is about the same as ε_1 without CI. The contribution ε_2 as compiled in Table 1 can then be determined. In BaF_2, the contribution from ε_1 is, like in $BaLiF_3$ and most likely generally in fluoride compounds, rather insignificant. The contribution rom the correlated motion between 5*d*-electron and ligand-electrons appears 10 times more important. In $LiYF_4$, computational problems arose in the calculation of the energies of higher lying 5*d*-orbitals because of the low symmetry at the fluorine sites. The value for ε_2 in Table 1 was based on a calculation on the lowest 5*d*-level only. Like for BaF_2 it demonstrates the important contribution from correlated motion.

In the oxides, ε_1 and ε_2 are of comparable magnitudes which demonstrates that as compared to the fluorides covalency becomes more important. Like for BaF_2, $\varepsilon_1 + \varepsilon_2$ is substantially smaller than the experimentally found centroid shift indicating that further improvements in theoretical modelling are still required. For yet unknown reasons the agreement appears better in $LaCl_3$ and $LaBr_3$ where, like in the oxides, ε_1 and ε_2 are of about equal magnitude.

The success in using Eq. (5) and the relationship between α_{sp} and cation electronegativity shown in Fig. 2, demonstrates that the correlated motion between 5*d* and ligand-electrons provides a very important contribution to the centroid shift. This is also demonstrated by the results from ab initio calculations compiled in Table 1. One should, however, regard the results in Table 1 as preliminary results expressing the present state of knowledge. It is anticipated that results can be improved by further optimizing the basis set and the cluster size in the HF-LCAO method.

Note the strong resemblance between the nephelauxetic *h*-parameter in Eq. (1) and the parameter *S* in Eq. (5). Both characterize the anion ligands and both tend to scale in accordance with the nephelauxetic series of Eqs. (2) and (3). However, *S* is also determined by the Ce to anion bondlengths, and actually α_{sp} appears to be the parameter that truly characterizes the anions. Based on the found relationship between α_{sp} and cation electronegativity, one may now order compounds in a sequence of increasing value for χ_{av}^{-2} as replacement for the series of Eq. (3). This works well for Ce^{3+}, see Fig. 2. The *k*-parameter in Eq. (1) is equivalent with σ in Eq. (5). σ is not expected to change much with the type of lanthanide ion [15]. Furthermore, experimental data give good evidence that the centroid shift of the 5*d*-configuration remains practically the same through the lanthanide series [16–20]. It is clear that the results obtained for Ce^{3+} in compounds should apply equally well to all other trivalent lanthanide ions. It is interesting to test to what extent the X_{av}^{-2} relationship applies to the *dd* transitions in transition metals, the *ff*-transitions in lanthanides, and the *sp*-transitions in the s^2-elements.

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