Relating the energy of the $[Xe]5d^1$ configuration of Ce^{3+} in inorganic compounds with anion polarizability and cation electronegativity

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Recently, the energy of all five levels of the $[Xe]5d$ configuration of Ce^{3+} in 63 different fluorides and oxides have become available. It provides values for the barycenter shift of the $5d$ configuration. This shift was analyzed by a model that involves the polarizability of the anion ligands, and values for the in-crystal anion polarizability were obtained. In this work, for Ce^{3+} in both the oxides and the fluorides, a linear relationship between the anion polarizability and the inverse square of the average electronegativity of the cations in the compounds is demonstrated. With few parameters, the magnitude of the nephelauxetic effect in inorganic compounds can now be predicted. More importantly, insights are provided on the relationship between physical and chemical properties of compounds and the luminescent properties of lanthanides.

I. INTRODUCTION

Many physical and chemical properties of inorganic compounds are determined by the bonding between the cations M and the anions X. When a second cation T is present, the T-X bond will modify the character of the M-X bond. If T is more electronegative than M, the anion will share its electrons preferentially with T and the M-X bond becomes more ionic, i.e., the counter cation T has an inductive effect on the M-X bond. Etourneau *et al.*[1] reviewed the important role of this inductive effect in solid-state chemistry.

The same effect is important in luminescence spectroscopy. Suppose a luminescence center is on the M cation site. Due to the crystal field, degenerate energy levels may split. In addition, levels may shift to lower energy by the so-called nephelauxetic effect.[2] For the dd transitions in the transition-metal elements and ff transitions in the lanthanides and actinides, the nephelauxetic effect is related to the reduction of the interelectron repulsion between the d or f electrons, respectively. This reduction is often attributed to covalency between luminescence center and the neighboring anions X.[2–4] The amount of covalency, i.e., the sharing of electrons between luminescence center and the neighboring anion X, is effected by the character of the counter cations. Here, the counter cations are defined as those cations, other than the luminescence center self, that coordinate the anion.

Theories developed for the $d^n \rightarrow d^n$ transitions and the $4f^n \rightarrow 4f^n$ transitions can also be applied to the $4f^n \rightarrow 4f^{n-1}5d^1$ transition in the lanthanides. However, there are some essential differences. The latter transition is between different configurations, and since there is only one single electron in the $5d^1$ configuration, interelectron repulsion between $5d$ electrons is absent.

This work deals with the interpretation of the nephelauxetic effect on the $4f \rightarrow 5d$ transitions in Ce^{3+} doped inorganic compounds. Compared to the other trivalent lanthanide ions, the energy-level structure of Ce^{3+} is simple. The ground-state electron configuration consists of the $[Xe]$ closed shell plus an optically active electron in the $4f$ shell. The $4f^1$ ground state is separated about $51\,000$ cm^{-1} from the excited $5d^1$ configuration. In a crystalline environment, the $5d$ configuration may split by as much as $25\,000$ cm^{-1} into at most five distinct $5d$ states. In addition the average energy of the five $5d$ levels may shift downwards by $22\,000$ cm^{-1}.[5–8] This downward shift is defined as the centroid shift ϵ_c of the $5d$ configuration. Although it is not solely caused by the genuine nephelauxetic effect,[9] this name is commonly used to express the shift.

Shift and splitting of the levels belonging to the $4f$ configuration are a factor of 20–50 less strongly influenced than those belonging to the $5d$ configuration. The reason is the effective shielding of the $4f$ electron from its environment by filled $5p$ and $5s$ shells. The centroid shift is therefore entirely determined by the interaction of one single $5d$ electron with its surrounding. Suppose Ce^{3+} is in a (hypothetical) state where the $5d$ electron is equally distributed over the five levels of the $5d$ configuration, then its charge cloud (in the free ion) will be spherically symmetric extending outside the $[Xe]$ core. With this in mind, the centroid shift provides a direct measure for the interaction of an (approximately) spherical symmetric charge cloud with the neighboring anions.

The centroid shift of Ce^{3+} in 17 different fluoride and 46 different oxide compounds were made available in a recent series of papers.[5–8] In those papers, a model was used that relates the centroid shift to the polarizability of the anion ligands. A correlation was demonstrated between the values derived for the anion polarizabilities and the type of cations in the compound. In this work, the influence of the cations on the polarizability of the anions is further analyzed. Both for Ce^{3+} in the fluoride and in the oxide compounds, an intriguing linear relationship between the average anion polarizability and an average cation electronegativity is demonstrated. It appears that based on the type of cations and the crystal structure alone the centroid shift of the Ce^{3+} $5d$ configuration in inorganic compounds can be predicted.

II. RESULTS AND DISCUSSION

Figure 1 displays the available data on the $5d$ centroid shift of Ce^{3+} in compounds as presented in Refs. 5–8. The
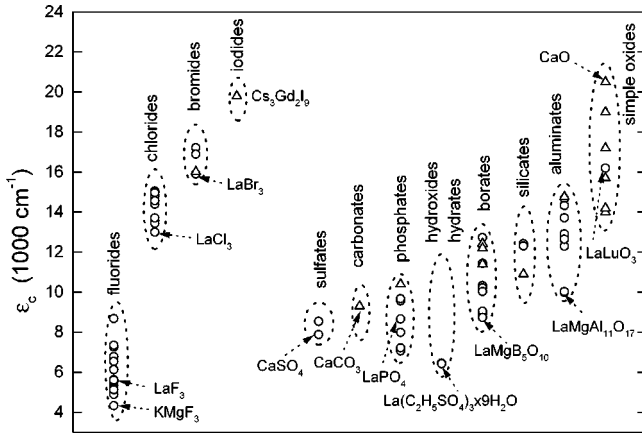
FIG. 1. The centroid shift ϵ_c (from Ref. 8) of the $5d$ configuration of Ce^{3+} in inorganic compounds. $\triangle$, are estimated values.

available data on the halides have been grouped into the fluorides, chlorides, bromides, and iodides. The centroid shift increases in the same sequence. The oxides are grouped into the sulfates, carbonates, phosphates, hydrated compounds, borates, silicates, aluminates, and the so-called "simple oxides." In the same sequence the centroid shift tends to increase. These trends correspond with the well-known nephelauxetic series for the halides and the complex groups in the oxides, and have been associated with the covalency between luminescence center and the anion ligands.[2]

Besides the covalency contribution to ϵ_c, there are contributions due to the overlap between $5d$ and anion ligands, see, e.g., Aull and Jenssen[10] and Andriessen et al.[11] They can be treated with standard Hartree-Fock-linear combination of atomic orbitals (HF-LCAO) theory using single electron operators. However, such theory appears not adequate to deal with highly ionic compounds like the fluorides where theoretically the centroid shift comes out much too small.[11,12] For the fluorides, Morrison[13] suggested another interaction, i.e., the $5d$-electron polarizes the ligand electrons, which in turn interact back on the $5d$ electron thus lowering its energy. In fact it describes a correlated motion between the $5d$ electron and the ligand electrons. It is a two-electron interaction, which can be dealt with by introducing two electron operators in the HF-LCAO theory. One may write

$$\epsilon_c = \epsilon_1 + \epsilon_2 \qquad (1)$$

to separate the contributions from single electron and two-electron interactions.

The two-electron contribution ϵ_2 can be calculated classically, and in first-order approximation one obtains[5,13]

$$\epsilon_2 = \frac{e^2}{4\pi\epsilon_0}(\langle r^2 \rangle_{5d} - \langle r^2 \rangle_{4f})\sum_{i=1}^{N}\frac{\alpha_i}{(R_i - f\Delta R)^6}, \qquad (2)$$

where r represents the position of the electron in either the $5d$ or $4f$ orbital, and $\langle r^2 \rangle$ is the expectation value of r^2. The values for the free Ce^{3+} ion will be used in this work.[5] α_i is the polarizability of ligand i located a distance R_i from Ce^{3+} in the unrelaxed lattice. The summation is over all N coordinating anion ligands. Since R_i enters as the sixth power in

Eq. (2), a correction for lattice relaxation around the Ce^{3+} ion must be made. However, for very few materials treated in this work detailed information on this relaxation is available. We will, therefore, assume that each anion relaxes radially by a fraction f of the difference ΔR in ionic radius between Ce^{3+} and the cation it substitutes for. To simplify matters further it will be assumed that α_i is equal for each anion.

There is no analytic expression available for ϵ_1 that allows simple calculation. In Refs. 5–8, a phenomenological approach was chosen. ϵ_2 in Eq. (2) was replaced by the experimentally observed centroid shift ϵ_c, and with R_i from the crystal structure and $f = 0.5$ the polarizability was calculated. Since its value was derived from spectroscopic information, it was denoted as the spectroscopic polarizability α_{sp}.[5] It relates to the actual polarizability as

$$\alpha_{sp} = \alpha\left(1 + \frac{\epsilon_1}{\epsilon_2}\right). \qquad (3)$$

The correction for lattice relaxation by introducing $f\Delta R$ is a crude approximation. Pedrini et al.[14] employed the same type of relaxation scheme for Tm^{2+} and Eu^{2+} in CaF_2, SrF_2, and BaF_2. Values for f between 0.5 and 0.75 were reported. Theoretical studies by Marsman et al.[12] on the relaxation around Ce^{3+} in BaF_2 showed that $f \approx 0.9$. The larger value is attributed to the excess positive charge on Ce^{3+}. Based on this, relatively large relaxation parameter f may be expected whenever Ce^{3+} substitutes a divalent site. The approximation of radial relaxation of the anions is expected to hold reasonably when the anion coordination around Ce^{3+} is regular and ΔR is not too large. In the case of $BaLiF_3:Ce^{3+}$, with large $\Delta R = 28$ pm, studies by Marsman et al.[12] showed severe distortions of the regular cuboctahedral fluorine coordination polyhedron around Ce^{3+}.

Despite the shortcoming of the relaxation model used in Eq. (2) all data on the centroid shift has been analyzed in this work assuming radial relaxation with $f = 0.6 \pm 0.1$. Values for ΔR where derived from the work by Shannon.[5,15] Refinements on the relaxation model can always be made afterwards when information is available on specific compounds. Table I compiles the centroid shift of the compounds together with α_{sp} calculated employing Eq. (2). The contribution to the error in α_{sp} due to Δf as compiled in Table I will vanish for La compounds, where ΔR is negligible. Note, that for these compounds α_{sp} is obtained without any freely chosen parameter whatsoever. For Ce^{3+} on a large cation site like Ba^{2+} or on a small cation site like Sc^{3+} the contribution to the error due to Δf may amount up to values larger than 0.1×10^{-30} m^3. For several compounds, spectroscopic information on Ce^{3+} $5d$ levels is incomplete. Nevertheless a fair estimate for the centroid shift could be made. α_{sp} values calculated from these estimated centroid shifts have errors of about $\pm 0.25 \times 10^{-30}$ m^3.

A qualitative relationship between α_{sp} and the electronegativity of the cations in compounds was already demonstrated in Refs. 5–8. The purpose of this work is to find a quantitative relationship. In this respect the work by Pearson provides an important clue.[16] Experimental data on the force

TABLE I. Centroid shift ϵ_c, average electronegativity χ_{av} of the cations in the compounds, and derived spectroscopic polarizabilities α_{sp}. Values on ϵ_c within brackets are estimated values.

Compound	ϵ_c (cm^{-1})	χ_{av}	α_{sp} (10^{-30} m^3)	Compound	ϵ_c (cm^{-1})	χ_{av}	α_{sp} (10^{-30} m^3)
Fluorides				$YMgB_5O_{10}$	8730	1.84	1.52±0.04
LuF_3	5130	1.27	0.72±0.03	GdB_3O_6	9050	1.83	1.72±0.04
YF_3	5630	1.22	0.80±0.02	$LaMgB_5O_{10}$	8950	1.83	1.77±0.01
$LiLuF_4$	5610	1.20	0.78±0.03	LaB_3O_6	8990	1.81	1.83±0.01
$NaMgF_3$	4890	1.18	0.79±0.01	$LuAl_3(BO_3)_4$	10 000	1.78	1.66±0.06
$BaLu_2F_8$	6130	1.18	0.87±0.04	$YAl_3(BO_3)_4$	10 200	1.78	1.75±0.05
$BaThF_6$	5580	1.16	0.82±0.05	$GdAl_3(BO_3)_4$	10 300	1.77	1.82±0.03
$LiYF_4$	5520	1.16	0.80±0.02	$ScBO_3$	(12 200)	1.70	1.98±0.2
$NaYF_4$	5630	1.15	0.89±0.06	Calcite-$LuBO_3$	(11 400)	1.66	2.12±0.15
$KMgF_3$	4330	1.15	0.83±0.06	Vaterite-$LuBO_3$	(12 400)	1.66	2.16±0.15
BaY_2F_8	6140	1.14	0.89±0.03	YBO_3	(12 400)	1.63	2.30±0.15
CeF_3	5350	1.12	0.88±0	$GdBO_3$	(12 400)	1.62	2.28±0.15
Rb_2NaScF_6	(8680)	1.11	1.07±0.14	$LaBO_3$	11 450	1.57	2.37±0.01
LaF_3	5580	1.10	0.94±0.00	$Li_6Y(BO_3)_3$	(12 730)	1.55	2.46±0.2
CaF_2	7350	1.00	1.11±0.01	Silicates			
SrF_2	7260	0.95	1.23±0.04	$Lu_2Si_2O_7$	12 421	1.63	2.23±0.09
$LiBaF_3$	6540	0.92	1.34±0.08	X2-Lu_2SiO_5	12 310	1.52	2.32±0.09
BaF_2	6780	0.89	1.52±0.10	$La_{4.67}(SiO_4)_3O$	(10 900)	1.50	2.36±0.01
Sulfates and carbonates				Aluminates			
$CaSO_4$	8630	2.19	1.70±0.02	$SrAl_{12}O_{19}$	10 000	1.58	2.29±0.05
$SrSO_4$	7930	2.17	1.79±0.03	$LaMgAl_{11}O_{19}$	10 000	1.55	2.37±0.01
$BaSO_4$	7840	2.01	1.98±0.12	$Y_3Al_5O_{12}$	14 700	1.46	2.72±0.08
$CaCO_3$	(9300)	2.03	1.88±0.2	$LuAlO_3$	12 650	1.44	2.13±0.09
Phosphates				$YAlO_3$	12 900	1.42	2.23±0.07
LaP_5O_{14}	7070	2.07	1.45±0.01	$GdAlO_3$	13 700	1.41	2.54±0.06
CeP_5O_{14}	7220	2.07	1.45±0	$LaAlO_3$	(14 800)	1.36	3.01±0.1
LaP_3O_9	7990	2.01	1.65±0.01	$CaYAlO_4$	14 300	1.31	3.13±0.3
$ScPO_4$	(10 500)	1.88	1.60±0.20	"Simple" oxides			
$LuPO_4$	9670	1.85	1.59±0.07	$La_2Be_2O_5$	(14 200)	1.29	3.07±0.2
YPO_4	9570	1.83	1.62±0.05	ThO_2	(15 700)	1.30	3.17±0.26
$LaPO_4$	8660	1.78	1.80±0.01	$SrHfO_3$	(14 600)	1.18	3.54±0.26
$K_3La(PO_4)_2$	8670	1.73	1.90±0.01	$CaZrO_2$	(17 200)	1.22	3.67±0.25
Aquo-compounds				$LaLuO_3$	16 200	1.19	3.76±0.1
$La(C_2H_5SO_4)_3\cdot 9H_2O$	6460	2.20	1.36±0.01	La_2O_3	(19 000)	1.1	4.34±0.4
Aqueous-$[Ce(OH_2)_9]^{3+}$	6420	2.20	1.33±0	CaO	(20 500)	1.00	5.00±0.4
Borates							

constant k of the metal-hydride bond in almost 50 different diatomic MH molecules were analyzed by Pearson. A proportional relationship between $\sqrt{k}$ and the value for the electronegativity χ of the metal atom was found.

In atomic physics, the polarizability α of an atom is related to the binding force constants k_i of its electrons as

$$\alpha \propto \sum \frac{1}{k_i}, \qquad (4)$$

where the summation is over all the electrons in the atom. This equation together with Pearsons finding suggests for binary M_xX_y compounds a relationship

$$\alpha_{sp} = \alpha_0 + \frac{b}{\chi^2}, \qquad (5)$$

where α_0 is the limiting polarizability in the case of very large χ, i.e., in the case of strong binding of the anion valence electrons to the metal. One might interpret b as the susceptibility of the anion to change its polarizability due to the binding with the metal. We will not comment further on its physical meaning since then one should also address the physical meaning of cation electronegativity.

To apply Eq. (5) to nonbinary compounds containing different cations, a suitable definition for the average cation electronegativity χ_{av} is needed. A cation of formal charge

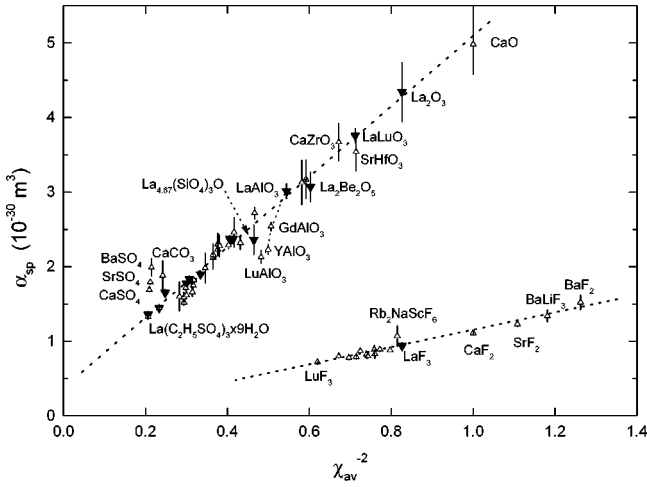FIG. 2. Spectroscopic polarizability determined, employing $f = 0.6 \pm 0.1$, from the centroid shift of the Ce^{3+} $5d$ configuration against the inverse square of the average cation electronegativity. Solid data symbols pertain to La-based compounds. The dashed lines are least-squares linear fits through the data (for the oxides the data on the La-based compounds were used).

$+z_i$ will bind on average with z_i/γ anions of formal charge $-\gamma$. The average is now defined as

$$\chi_{av} = \frac{1}{N_a} \sum_i^{N_c} \frac{z_i \chi_i}{\gamma}, \tag{6}$$

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.

With Pauling type[17] electronegativity values χ_i as compiled by Allred,[18] χ_{av} was determined for each compound, see Table I. For example, $\chi_{CaSO_4} = (2\chi_{Ca} + 6\chi_S)/8$. For $La(C_2H_5SO_4)_3 \times 9H_2O$, where the Ce^{3+} ion on the La^{3+} site is coordinated by neutral water molecules,[7] χ_{av} was assumed to be equal to the electronegativity of the hydrogen atom.

Figure 2 shows α_{sp} against the inverse square of the average cation electronegativity. It reveals, both for the oxide and the fluoride compounds, a good linearity in accordance with Eq. (5). Most compounds fall within error to the drawn dashed lines. Deviations may well be caused by contributions, other than compiled in Table I, to the errors in the values for α_{sp}. The largest error comes from the unknown lattice relaxation around Ce^{3+}, which may be different than assumed in Eq. (2). This may be the case for $GdAlO_3$, $YAlO_3$, and $LuAlO_3$. In this sequence their perovskite lattice structure, almost regular for $LaAlO_3$, collapses progressively and coordination around the lanthanide site becomes highly irregular with quite distant and very nearby anion neighbors.[8] If the too large Ce^{3+} ion is located on such site, the relaxation around Ce^{3+} needs not be radial as assumed in Eq. (2). Likely the nearest anions will relax further outward than estimated with $f = 0.6$. The most distant ones may even relax inward ($f < 0$). An off-center location of Ce^{3+} is also thinkable. In both cases α_{sp} will be calculated larger and data in Fig. 2 will deviate less. The relatively large positive devia-
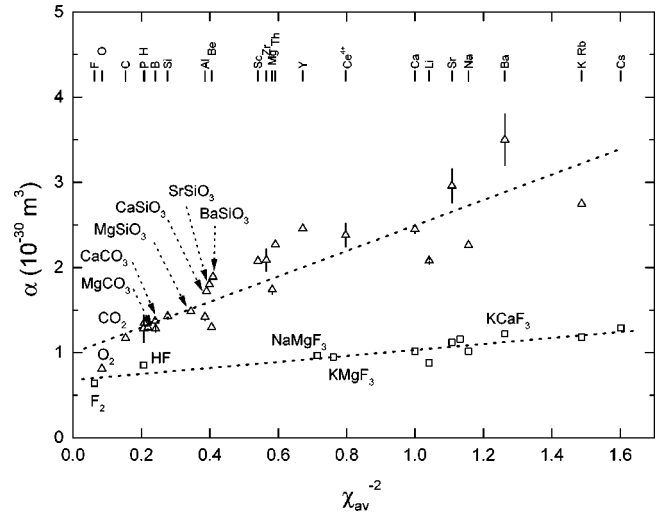

FIG. 3. In-crystal anion polarizability determined from the index of refraction. The vertical bars in the top part of the figure indicate the location on the χ_{av}^{-2} axis of data belonging to binary $M_x X_y$ compounds. The dashed lines are least-squares linear fits through the data.

tion for $CaSO_4$, $SrSO_4$, $BaSO_4$, and $CaCO_3$ may well be caused by the excess charge of Ce^{3+} leading to a stronger attraction, i.e., $f > 0.6$, of the nearby anions. An enhanced value for α_{sp} due to a nearby charge compensating defect is also not excluded.

Another source of error is in the definition of χ_{av}. For example, there are two different sites for La^{3+} in the apatite structure of $La_{4.67}(SiO_4)_3O$. Ce^{3+} on the one site is likely to interact differently with its neighbors than on the other site.[7] With the definition in Eq. (6) discrimination between sites is not made. One may also think of other definitions for χ_{av}, like averaging without using z_i as a weighting factor. The data was also analyzed with this alternative. For the binary compounds and compounds with two types of cations of the same ionic charge or about equal electronegativity χ_{av} it will not make any difference. For the compounds with cations with very different ionic charge like $Li_6Y(BO_3)_3$ and $K_3La(PO_4)_2$ or for compounds with very different χ_i like $BaSO_4$ and $SrSO_4$, somewhat different values for χ_{av} are obtained. However, the general appearance as in Fig. 2 remains quite the same with unaltered slopes of the dashed straight lines.

It is interesting to compare α_{sp} with actual anion polarizabilities experimentally determined from the refractive index of compounds. Figure 3 displays information on α available for compounds and molecules as reported in literature. Data on alkaline[19,20] and alkaline earth[20] fluorides and $KCaF_3$, $KMgF_3$, and $NaMgF_3$ (Ref. 21) scale linearly with χ_{av}^{-2}, nicely extrapolating through the data belonging to the HF and the F_2 $[\alpha(F^-) = 1/2\alpha(F_2)]$ molecules.[22]

The data on the oxides pertain to binary compounds from Refs. 20, 23, 24, the compounds $CaCO_3$ and $MgCO_3$,[25] and the metasilicates $MSiO_3$ ($M = Mg, Ca, Sr, Ba$).[26,27] Of the polarizability of the molecules CO_2,[28] O_2, and H_2O, respectively 50%, 50% and following Alkorta et al.[29] 78% is as-

sumed to reside on the oxygen ligand. The error in polarizability α is not known, but it can be quite substantial especially in compounds with cations of small electronegativity. The errors occasionally shown in Fig. 3 indicate the range of values reported for the same compound by different sources.

Although the scatter is quite substantial, especially for the alkali oxides, the oxygen polarizability tends to scale linearly with χ_{av}^{-2}. The slope $b = 1.5$, see Eq. (5), is 4.2 times larger than in the case of the fluorides. The same ratio is observed for α_{sp} where for oxides and fluorides the slopes are $b = 4.7$ and $b = 1.2$, respectively. Note that the variation of α_{sp} with χ_{av}^{-2} is three times stronger than that of α. One may suggest that the contribution ϵ_1 from the single electron interactions like covalency to the centroid shift is much larger than the contribution ϵ_2 from anion polarizability. However, this seems not to be the case.

Based on the new insights regarding the two electron interactions, we recently performed calculations on the centroid shift of the $5d$ levels of Ce^{3+} in BaF_2, LaAlO_3, and LaCl_3 using the ionic cluster approach.[11] By applying configuration interaction as extension of the basic HF-LCAO approach and with a basis set optimized for polarization of the anions, the effects of anion polararizability on the centroid shift were calculated. The ratio ϵ_1/ϵ_2 appears 0.1, 0.6, and 1.0 for BaF_2, LaAlO_3, and LaCl_3, respectively. Clearly the two-electron contribution is the most important contribution to the centroid shift in oxides and especially the fluorides. Several other reasons for the factor of three difference between α_{sp} and actual anion polarizability α can be thought of (1) a possible dispersion of polarizability with wavelength. The anion polarizabilities in Fig. 3 are derived from optical studies on the length scale of ≈ 500 nm whereas α_{sp} pertains to polarizability on the atomic length scale of about 500 pm. (2) For $\langle r_{5d}^2 \rangle$ in Eq. (2) the free ion value was used. In compounds, charge cloud expansion will increase this ex-

pectation value. (3) Equation (2) is a first-order approximation based on classical physics. One may not expect an accurate description for the centroid shift.

The arguments and analyzis leading to the linear relationship between α_{sp} and χ_{av}^{-2} has been entirely based on the two electron interaction involving anion polarizability. However, for oxide compounds the single electron contribution ϵ_1 is quite significant, i.e., $\approx 40\%$ in the case of LaAlO_3. The fact that still a linear relationship is observed in Fig. 2 suggests that the ratio ϵ_1/ϵ_2, see Eq. (3), remains more or less constant for all oxide compounds. Future theoretical calculations on other oxides than LaAlO_3 are needed to verify this.

III. SUMMARY

A relationship has been demonstrated between the centroid shift of the $5d$ configuration of Ce^{3+}, the polarizability of the anions, and the electronegativity of the cations in compounds. Without the use of any freely chosen parameter, values representing the polarizability of the anions were calculated from the observed centroid shift that correlate well with actual in crystal anion polarizabilities. Both scale linearly with the inverse square power of the average cation electronegativity. This relationship is of value for the interpretation and prediction of spectroscopic properties involving Ce^{3+} in compounds. Since the centroid shift of the $4f^n5d^1$ configuration in all other trivalent lanthanides is expected to be the same as in Ce^{3+},[30,31] the relationship should apply equally well to those other lanthanides.

A small value of the spectroscopic polarizability α_{sp} indicates a strong binding of the anion ligands by the counter cations. One may, therefore, regard α_{sp} as a quantitative measure for the inductive effect of these counter cations, and in the present work a simple quantitative relationship with the electronegativity of the cations has been established. Since the inductive effect plays an important role in solid-state chemistry,[1] ideas in this work may be applied there also.

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