

Spectral-line-broadening study of the trivalent lanthanide-ion series. II. The variation of the electron-phonon coupling strength through the series

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(Received 15 May 1996)

The variation of an electron-phonon coupling strength of lanthanide ions is evaluated by measuring the temperature-dependent line broadening of a large number of $4f$ transitions of nine lanthanide ions. The results show that the electron-phonon coupling strength derived from these line-broadening experiments is large in the beginning ($\text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}$) and the end ($\text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}$) of the trivalent lanthanide-ion series, but small at the center ($\text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$). This trend can qualitatively be explained by the lanthanide contraction and the shielding of the $4f$ electrons. [S0163-1829(97)00201-4]

I. INTRODUCTION

The shielding of the $4f$ electrons of trivalent lanthanide ions by the outer $5s^2$ and $5p^6$ electrons give the luminescence spectra of lanthanide ions their characteristic appearance: sharp line spectra which resemble the atomic (gas) spectra. The interaction of the $4f$ electrons with their surroundings is well known to be weak due to the shielding. Still, electron-phonon coupling is present and this interaction is responsible for important phenomena like multiphonon relaxation, vibronic transitions, line broadening, and (phonon-assisted) energy-transfer processes.⁴⁸ These phenomena have been the subject of study for decades. However, the question whether there is a systematic variation of an electron-phonon coupling strength through the lanthanide series, is fascinating and not fully answered yet.

In a few studies answers to this question can be found. For example, the energy-gap law for multiphonon relaxation assumes that the multiphonon relaxation transition probabilities depend only on the required number of phonons and on the energy gap between the two levels between which the radiationless relaxation occurs.^{1,2} This means that in the energy-gap law it is assumed that there is no difference in electron-phonon coupling strength for the different lanthanide ions.³ In more recent models for multiphonon relaxation (see for example Refs. 3 and 4) parameters depending on the lanthanide ions are introduced. However, up till now, this has not led to a further understanding of a possible variation of the electron-phonon strength through the trivalent lanthanide-ion series.

Next to multiphonon relaxation, the electron-phonon coupling manifests itself also in vibronic transitions. From measurements on vibronic transitions of Pr^{3+} and Gd^{3+} , it was derived that the vibronic transition probability (A_{vib}) for the former is more than one order of magnitude larger than for the latter. This was explained by the lanthanide contraction and the difference in admixture of the $4f^{n-1}5d^1$ states. Hence, it was predicted that an increase in vibronic coupling strength from Gd^{3+} to Tm^{3+} is unlikely.^{5,6} Based on the lanthanide contraction, one would expect a gradual decrease of the electron-phonon coupling strength through the lanthanide-ion series.

However, in contrast to these results, recent measurements on the vibronic transitions of Tm^{3+} in LiYF_4 show that the vibronic transition probabilities of Tm^{3+} are of a magnitude comparable to those of Pr^{3+} .⁷ This indicates that the electron-phonon coupling strength through the trivalent lanthanide-ion series shows a symmetric behavior: strong in the beginning and the end of the series, and weak in the middle. It has been suggested that this behavior of the electron-phonon coupling strength could be explained by considering the shielding (σ_2) of the $4f$ electrons. A disadvantage of the method of using vibronic transition probabilities to evaluate an electron-phonon coupling strength is that reliable values of the vibronic transition probabilities are difficult to determine for many trivalent lanthanide ions.⁷

The symmetric behavior of the electron-phonon coupling strength of trivalent lanthanide ions was suggested earlier by Hellwege^{8,9} and Krupke.^{10,11} Hellwege derived this in 1941 from linewidth measurements at 80 K, the relative intensity of vibronic lines, the luminescence output, and the mean crystal-field splitting of the energy levels. He performed measurements on $L_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ salts ($L = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er},$ and Tm), and found a strong electron-phonon coupling in the beginning of the series (Pr^{3+} and Nd^{3+}), a weak coupling in the middle ($\text{Eu}^{3+}, \text{Gd}^{3+}$) and a strong coupling, but weaker than in the beginning, at the end of the series (Er^{3+} and Tm^{3+}). He suggested to explain this peculiar symmetry through the lanthanide series by the symmetry in the total spin quantum number S of the ions.

The data Hellwege presented are limited, but the same variation was also found by Krupke in 1966.^{10,11} He based his conclusion on the intense vibronic transitions he observed for $\text{Pr}^{3+}(4f^2)$ and $\text{Tm}^{3+}(4f^{12})$, weaker vibronic transitions for $\text{Nd}^{3+}(4f^{3+})$ and $\text{Er}^{3+}(4f^{11})$ and the absence of these for $\text{Eu}^{3+}(4f^6)$. The host lattice in this case was Y_2O_3 (C_2 site). Unfortunately, he did not show spectra, nor did he calculate vibronic transition probabilities. Krupke ascribed the variation of the electron-phonon coupling to the behavior of the experimental Judd-Ofelt parameters Ω_2 , Ω_4 , and Ω_6 .

Summarizing, the electron-phonon coupling does either *not* depend on the lanthanide ion (simple energy-gap law for multiphonon relaxation), or it decreases through the lanthanide series (Ref. 5), or it shows a symmetric behavior around the half-filled shell configuration (according to Hell-

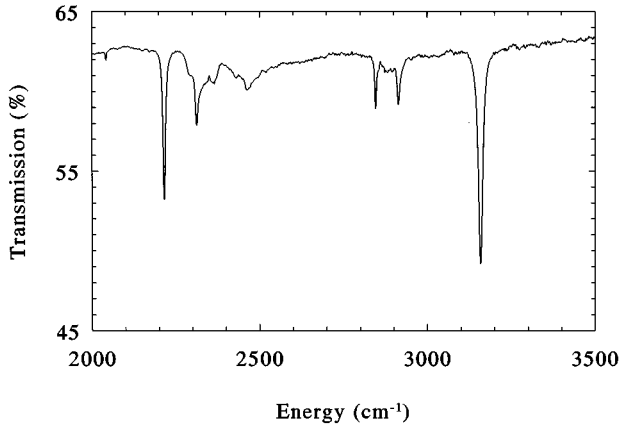


FIG. 1. Absorption spectrum at 100 K of single crystalline $\text{LiYF}_4:\text{Ce}^{3+}$.

wege and Krupke^{8–11}). Next to these three possibilities, it might also be proposed that there is no variation at all because there are too many parameters influencing the electron-phonon coupling.

It is clear that these conflicting results and ideas on the variation of the electron-phonon coupling strength in the lanthanide-ion series are a good reason to study this phenomenon in more detail. To study the variation of an electron-phonon coupling strength the linewidth was measured as a function of temperature for many intraconfigurational $4f^n$ transitions of nine trivalent lanthanide ions in LiYF_4 .

This line-broadening study is divided into two parts. In the first part (the previous paper) it was shown that the method of line-broadening measurements is a reliable and relatively easy method to probe an electron-phonon coupling strength of different lanthanide ions. This method is used in this paper (part II) to investigate the electron-phonon coupling strength for nine lanthanide ions (Ce^{3+} , Pr^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+}). The aim of our research is to derive from these linewidth measurements an answer to the question whether or not there is a trend of the electron-phonon coupling strength through the trivalent lanthanide-ion series. Part of the results obtained by this method were presented earlier at the DPC'95.¹² Now a more elaborate overview and discussion of the results is given and recently obtained data are included.

II. EXPERIMENT

Single crystals of LiYF_4 were grown, using the Bridgman method, with Ce^{3+} , Pr^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} as dopant ions. The crystal growth melt contained 0.05 at. % of dopant ion. The crystals were transparent. Pieces of some 1.5 mm thick were used for the measurements. Crystalline powders of LiYF_4 with the dopant ions Nd^{3+} , Eu^{3+} , Gd^{3+} , and Tb^{3+} were prepared according to the procedure described in Refs. 13 and 14. The samples were checked by x-ray powder-diffraction analysis and found to be single phase. Transmission spectroscopy showed that the samples did not contain optical impurities.

High-resolution excitation and emission measurements were done with an excimer-laser-pumped dye laser and a Nd:YAG laser setup.¹² The IR absorption spectra of the $4f$

TABLE I. $\bar{\alpha}$ values obtained for the transitions studied of Ce^{3+} in LiYF_4 . $\sigma = \sum_i |\text{fit value}_i - y_i| / \sum_i y_i$.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^2F_{5/2} \leftarrow {}^2F_{7/2}$	2216	300	0.05
${}^2F_{5/2} \leftarrow {}^2F_{7/2}$	3160	145	0.06

transitions of the Ce^{3+} -containing crystal were measured between 100 and 303 K in transmission with a Perkin-Elmer 1720-X infrared Fourier-transform spectrometer; the resolution of this setup is better than 2 cm^{-1} . The data manipulation was done with PE Grams Research Galactic Software.

III. RESULTS AND DISCUSSION

In this section the results of the line-broadening study of nine different lanthanide ions are presented. The temperature-dependent linewidth (full width at medium height) data are fitted according to the following equation:

$$\Delta E(T) = E^{\text{inh}} + E^R(T) = E^{\text{inh}} + \bar{\alpha} \left(\frac{T}{T_D} \right)^7 \int_0^{T_D/T} \frac{x^6 e^x}{(e^x - 1)^2} dx. \quad (1)$$

Here, E^{inh} is the inhomogeneous linewidth and $E^R(T)$ the contribution to the linewidth of the Raman two-phonon process. $\bar{\alpha}$ is the electron-phonon coupling parameter for the Raman process, T_D is the effective Debye temperature and $x = \hbar \omega / kT$. In the previous paper (part I) it has been shown that this formula presents a satisfying approximation of the temperature dependence of the linewidth and that it can be used to estimate the electron-phonon coupling strength of intraconfigurational $4f^n$ transitions of lanthanide ions. Equation (1) is applied to describe the temperature-dependent linewidth of both Kramers and non-Kramers ions, although the matrix elements hidden in $\bar{\alpha}$ are different for these ions.

A. $\bar{\alpha}$ values

1. Ce^{3+} ($4f^1$)

Most spectroscopic research on Ce^{3+} (see, for example, Refs. 15–19) has been performed on the $4f$ - $5d$ transitions of this ion. Here the transition ${}^2F_{5/2} \leftarrow {}^2F_{7/2}$ within the $4f^1$ configuration of Ce^{3+} in LiYF_4 is measured (see Fig. 1). Unfortunately, our spectroscopic study was hampered by several problems. It was not possible to measure with polarized light and the temperature could only be varied between 100 and 303 K. This means that it is impossible to assign the ob-

TABLE II. $\bar{\alpha}$ values obtained for the transitions studied of Pr^{3+} in LiYF_4 . The transitions are assigned according to Ref. 23.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^3P_{0A} \Rightarrow {}^3H_{6B}$	16 549	153	0.15
${}^3P_{0A} \Rightarrow {}^3H_{6C}$	16 472	111	0.05
${}^3P_{0A} \Rightarrow {}^3H_{4C}$	20 787	88	0.05
${}^3P_{0A} \leftarrow {}^3H_{4B}$	20 871	63	0.06
${}^1D_{2B} \Rightarrow {}^3H_{4C}$	16 667	161	0.06
${}^3P_{0A} \Rightarrow {}^3F_{2B}$	15 640	30	0.09

TABLE III. $\bar{\alpha}$ values obtained for the transitions studied of Nd^{3+} in LiYF_4 . The transitions are assigned according to Ref. 25.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^2P_{3/2}(\Gamma_{7,8}) \Rightarrow {}^4I_{9/2}(\Gamma_{7,8})$	26 295	51	0.232
${}^2P_{3/2}(\Gamma_{7,8}) \Rightarrow {}^4I_{11/2}(\Gamma_{7,8})$	24 297	48	0.226

served transitions. Next to these instrumental problems, the IR transmission spectrum is obscured by CO_2 absorption and extra lines in the 2800–2900 cm^{-1} region. Those lines were also present in the IR absorption spectra of other $\text{LiYF}_4:\text{L}^{3+}$ crystals and are of an unknown origin. When the transmission spectrum is compared to those of other $\text{LiYF}_4:\text{L}^{3+}$ crystals, it can be concluded that two intense lines in Fig. 1 are characteristic for the Ce^{3+} -doped crystal and that they can be attributed to the intraconfigurational $4f^1$ transitions of Ce^{3+} . These lines (at 2216 and 3160 cm^{-1}) are well separated from the other absorptions and can be utilized for temperature-dependent linewidth measurements. The $\bar{\alpha}$ values, derived from a fit of the line-broadening data of these two transitions to Eq. (1), are presented in Table I.

2. Pr^{3+} ($4f^2$)

The linewidth data on $\text{LiYF}_4:\text{Pr}^{3+}$ were presented in the previous paper (part I): they are summarized in Table II. The linewidth behavior and the obtained $\bar{\alpha}$ values are in line with the line-broadening measurements performed on Pr^{3+} in other crystalline materials like LaF_3 and LiLuF_4 .^{20–22}

3. Nd^{3+} ($4f^3$)

Only two transitions were studied on Nd^{3+} in LiYF_4 : the ${}^2P_{3/2}(\Gamma_{7,8}) \Rightarrow {}^4I_{9/2}(\Gamma_{7,8})$ transition at 26 295 cm^{-1} and the ${}^2P_{3/2}(\Gamma_{7,8}) \Rightarrow {}^4I_{11/2}(\Gamma_{7,8})$ transition at 24 297 cm^{-1} . The $\bar{\alpha}$ values for these transitions are some 51 and 48 cm^{-1} , respectively (see Table III). These values are lower than most of the $\bar{\alpha}$ values for Pr^{3+} and Ce^{3+} . A smaller line broadening with temperature for Nd^{3+} than for Pr^{3+} is in line with results of line-broadening studies on these ions in LaF_3 (Refs. 24 and 20, respectively).

4. Eu^{3+} ($4f^6$)

The line-broadening results of $\text{LiYF}_4:\text{Eu}^{3+}$ were presented in part I of these papers; in Table IV the $\bar{\alpha}$ values for several transitions are tabulated. It is clear that the electron-

TABLE IV. $\bar{\alpha}$ values obtained for the transitions studied of Eu^{3+} in LiYF_4 . The transitions are assigned according to Ref. 26.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^5D_1(\Gamma_1) \Leftarrow {}^7F_0(\Gamma_1)$	19 048	4.8	0.06
${}^5D_1(\Gamma_{3,4}) \Leftarrow {}^7F_0(\Gamma_1)$	19 025	4.2	0.11
${}^5D_0(\Gamma_1) \Rightarrow {}^7F_1(\Gamma_1)$	16 847	17.2	0.11
${}^5D_0(\Gamma_1) \Rightarrow {}^7F_2(\Gamma_2^2)$	16 385	23	0.10
${}^5D_0(\Gamma_1) \Rightarrow {}^7F_2(\Gamma_{3,4})$	16 313	27	0.08
${}^5D_0 \Rightarrow {}^7F_{3,4}$		4–40	
${}^5D_1 \Rightarrow {}^7F_{2,3}$		4–40	

TABLE V. $\bar{\alpha}$ values obtained for the transitions studied of Gd^{3+} in LiYF_4 .

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^6P_{7/2} \Rightarrow {}^3S$	32 118	3.5	0.04
${}^6P_J, {}^6I_J \Rightarrow {}^8S$		3–20	

phonon coupling strength of Eu^{3+} in LiYF_4 , as derived from these line-broadening experiments, is much smaller than those of the lighter lanthanide ions Ce^{3+} , Pr^{3+} , and Nd^{3+} . Next to the transitions studied in the temperature domain between 4.2 and 300 K (Table IV), we have measured the linewidth at 4.2 and 300 K of several ${}^5D_1 \Rightarrow {}^7F_{2,3}$ and ${}^5D_0 \Rightarrow {}^7F_{3,4}$ transitions. Although no $\bar{\alpha}$ values can be derived from data measured at only two temperatures, it could be estimated that the $\bar{\alpha}$ values vary between 4 and 40 cm^{-1} .

5. Gd^{3+} ($4f^7$)

For $\text{LiYF}_4:\text{Gd}^{3+}$ only one transition was studied: ${}^6P_{7/2} \Rightarrow {}^8S_{7/2}$. The $\bar{\alpha}$ value obtained for this transition is very small, viz. 3.5 cm^{-1} (see Table V). The presence of a minimum in the electron-phonon coupling strength in the center of the series is confirmed by linewidth measurements on all ${}^6P_J, {}^6I_J \Rightarrow {}^8S_{7/2}$ transitions at 300 K. The linewidth of these transitions at 300 K is less than 7 cm^{-1} , which is much smaller than for the transitions of Pr^{3+} , which are at 300 K between 20 and 50 cm^{-1} . The $\bar{\alpha}$ values, estimated from the linewidths of all ${}^6P_J, {}^6I_J \Rightarrow {}^8S_{7/2}$ transitions at room temperature, are between 3 and 20 cm^{-1} .

6. Tb^{3+} ($4f^8$)

The line broadening of a large number of transitions of $\text{LiYF}_4:\text{Tb}^{3+}$ have been studied. However, the study of the temperature-dependent line broadening is complicated by the fact that a large number of terms of the Tb^{3+} ion have many closely spaced crystal-field components. At low temperatures this does not hamper a reliable fit of the line width data but at elevated temperatures, when also energetically higher

TABLE VI. $\bar{\alpha}$ values obtained for the transitions studied of Tb^{3+} in LiYF_4 . The transitions are assigned according to Refs. 25 and 27.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^5D_4 \Rightarrow {}^7F_3$	16 142	20	0.11
	16 175	21	0.14
	16 233	28	0.15
${}^5D_4 \Leftarrow {}^7F_6$	20 572	96	0.06
	20 638	108	0.05
${}^5D_3 \Rightarrow {}^7F_4$	22 936	38	0.12
	22 985	44	0.08
	23 010	51	0.16
	23 017	43	0.10
	23 043	49	0.08
${}^5D_3 \Rightarrow {}^7F_5$	24 170	70	0.09
	24 242	65	0.09
${}^5L_J \Leftarrow {}^7F_6$	27 913	86	0.08

TABLE VII. $\bar{\alpha}$ values obtained for the transitions studied of Er^{3+} in LiYF_4 . The transitions are assigned according to Refs. 25 and 28–30.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^4I_{11/2}(1) \Rightarrow {}^4I_{15/2}(1)$	10 218	37	0.03
${}^4I_{11/2}(1) \Rightarrow {}^4I_{15/2}(2)$	10 201	27	0.04
${}^4I_{11/2}(5) \Leftarrow {}^4I_{15/2}(1)$	10 321	31	0.19
${}^4I_{9/2}(1) \Leftarrow {}^4I_{15/2}(1)$	12 361	36	0.09
${}^4S_{3/2}(1) \Rightarrow {}^4I_{15/2}(4)$	18 378	47	0.12
${}^2P_{3/2}(1) \Rightarrow {}^4I_{11/2}(?)$	21 288	16	0.08
${}^4F_{5/2}(?) \Leftarrow {}^4I_{15/2}(1)$	22 287	39	0.06
${}^4F_{5/2}(?) \Leftarrow {}^4I_{15/2}(1)$	22 297	46	0.09
${}^4F_{5/2}(?) \Leftarrow {}^4I_{15/2}(1)$	22 311	38	0.06

crystal-field components are thermally occupied, too many transitions are found in a small region to obtain reliable fits of the data. This spectroscopic drawback is compensated by measuring a large number of transitions. The $\bar{\alpha}$ values obtained from the temperature-dependent line-broadening measurements are given in Table VI. In view of the available literature data,^{25,27} a more detailed assignment of the transitions than given in Table VI was not possible. It is clear that the $\bar{\alpha}$ values for the transitions on Tb^{3+} are larger than those for Eu^{3+} , but they are smaller than those for Pr^{3+} .

7. Er^{3+} ($4f^{11}$)

The $\bar{\alpha}$ values obtained for the studied transitions of $\text{LiYF}_4:\text{Er}^{3+}$ are given in Table VII. The assignment of the transitions is according to Refs. 25 and 28–30. The transitions in which the ${}^4F_{5/2}$ and ${}^2P_{3/2}$ states are involved cannot be assigned unambiguously. The electron-phonon coupling strength $\bar{\alpha}$ of Er^{3+} is small, although larger than for Gd^{3+} .

8. Tm^{3+} ($4f^{12}$)

The $\bar{\alpha}$ values derived from the line-broadening experiments on $\text{LiYF}_4:\text{Tm}^{3+}$ are summarized in Table VIII. The assignment of the transitions is according to Refs. 25, 31, and 32. There is also a rather large variation of $\bar{\alpha}$ values for different transitions. This fact stresses the necessity to measure a large number of transitions to obtain a reliable measure of the electron-phonon coupling strength of an individual ion.

TABLE VIII. $\bar{\alpha}$ values obtained for the transitions studied of Tm^{3+} in LiYF_4 . The transitions are assigned according to Refs. 25, 31, and 32.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^1D_2(1) \Rightarrow {}^3F_4(2)$	22 210	82	0.13
${}^1D_2(1) \Rightarrow {}^3F_4(1)$	22 370	149	0.07
${}^1D_2(2) \Rightarrow {}^3F_4(1)$	22 404	63	0.15
${}^1G_4(1) \Rightarrow {}^3H_6(2)$	20 953	119	0.08
${}^1G_4(2) \Rightarrow {}^3H_6(3)$	21 143	196	0.09
${}^1G_4(2) \Rightarrow {}^3H_6(2)$	21 166	146	0.02
${}^1G_4(1) \Rightarrow {}^3H_6(1)$	21 196	327	0.03

TABLE IX. $\bar{\alpha}$ values obtained for the transitions studied of Yb^{3+} in LiYF_4 . The transitions are assigned according to Ref. 25.

Transition	Energy (cm^{-1})	$\bar{\alpha}$ (cm^{-1})	σ
${}^2F_{5/2}(1) \Rightarrow {}^2F_{7/2}(3)$	10 046	355	0.12
${}^2F_{5/2}(1) \Leftarrow {}^2F_{7/2}(1)$	10 289	247	0.05
${}^2F_{5/2}(2) \Leftarrow {}^2F_{7/2}(1)$	10 412	278	0.02

9. Yb^{3+} ($4f^{13}$)

The last ion which we have investigated in the scope of this electron-phonon coupling study is Yb^{3+} . The $\bar{\alpha}$ values for the three transitions between crystal-field components of the two $4f^{13}$ states (${}^2F_{5/2}$ and ${}^2F_{7/2}$) of Yb^{3+} that were studied are given in Table IX. The assignment of the transitions is according to Ref. 25. From the $\bar{\alpha}$ values it can be derived that Yb^{3+} has a relatively strong electron-phonon coupling. A strong electron-phonon coupling strength has also been observed in other samples reported in the literature (see for example Refs. 33 and 34).

B. General discussion

A compilation of all $\bar{\alpha}$ values found in the Tables I–IX is shown in Fig. 2. Although it is well known that the electron-phonon coupling strength of the trivalent lanthanide ions is weak, the data show clearly that within this range of small electron-phonon coupling strength values, there is a significant variation. For both Kramers and non-Kramers ions applies: the electron-phonon coupling is strong in the beginning and at the end of the series, and weak in the middle.

This leaves us with the question how to explain this trend in the electron-phonon coupling strength $\bar{\alpha}$. In the introduction it was mentioned that Hellwege^{8,9} and Krupke^{10,11} found a similar variation of the electron-phonon coupling strength through the trivalent lanthanide ion series. Their conclusion was based on a relatively small number of data on different spectroscopic phenomena (luminescence intensity, crystal-field splitting, vibronic sidebands, linewidth at 80 K). Here this variation of the electron-phonon coupling strength is obtained with a rather large number of data, and is proved with another method than theirs: temperature-dependent line-broadening measurements. A large number of data for one

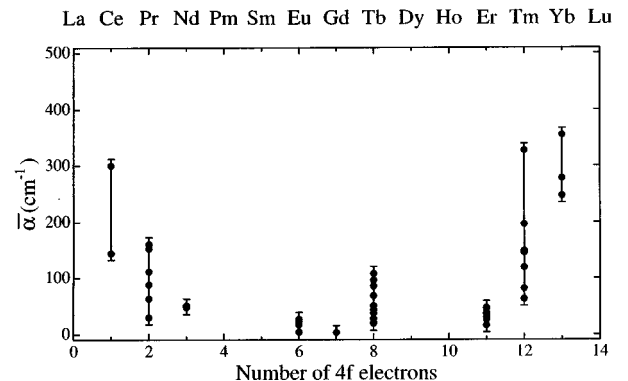


FIG. 2. $\bar{\alpha}$ values of the intraconfigurational $4f$ transitions of trivalent lanthanide ions in LiYF_4 . This figure is a compilation of the $\bar{\alpha}$ values for all the measured transitions (see Tables I–IX).

TABLE X. Experimental Judd-Ofelt Ω_λ parameters of Pr^{3+} , Gd^{3+} , and Tm^{3+} in LiYF_4 .

System	Ω_2 (10^{-20} cm ²)	Ω_4 (10^{-20} cm ²)	Ω_6 (10^{-20} cm ²)	Reference
$\text{LiYF}_4:\text{Pr}^{3+}$	0	8.07	7.32	23
$\text{LiYF}_4:\text{Gd}^{3+}$	0.32		1.8	35–37
$\text{LiYF}_4:\text{Tm}^{3+}$	2.43	1.08	0.67	32

ion is important, since the electron-phonon coupling strength for different transitions on one ion can vary considerably. Conclusions on the electron-phonon coupling strength based on a limited number of data might give a wrong idea of the variation of the electron-phonon coupling strength through the lanthanide-ion series.

Hellwege tried to explain the symmetric behavior of the electron-phonon coupling strength by the symmetry of the total spin quantum number S , but he did not give a physical model on how the variation of the total spin quantum number S would influence the electron-phonon coupling strength.

Krupke explained the variation of the electron-phonon coupling strength (as derived from vibronic sidebands), by the behavior of the experimental Judd-Ofelt parameters Ω_2 , Ω_4 , and Ω_6 . He found that the Ω_4 and Ω_6 parameters of the lanthanide ions in Y_2O_3 (C_2 site) are large in the beginning and at the end of the series and smaller in the middle. Therefore, it might be worthwhile to compare these parameters for different lanthanide ions in LiYF_4 in order to investigate if there is a correlation too. In literature only data for $\text{LiYF}_4:\text{Pr}^{3+}$ (Ref. 23) and $\text{LiYF}_4:\text{Tm}^{3+}$ (Ref. 32) were found; from the data given by Sytsma and co-workers in Refs. 35–37 the values of Ω_2 and Ω_6 for $\text{LiYF}_4:\text{Gd}^{3+}$ can be derived (see Table X). It is clear from this table that the Ω_λ values of Pr^{3+} and Gd^{3+} and Tm^{3+} in LiYF_4 do not follow the same variation as in Y_2O_3 . This suggests that the variation of the Ω_λ parameters does not follow the variation of the electron-phonon coupling strength. In Refs. 38–40 the Ω_λ parameters for trivalent lanthanide ions in other host lattices [like YAlO_3 , LaF_3 , and $\text{NaLa}(\text{MoO}_4)_2$] are reported. Also in these lattices the variation in the Ω_λ parameters as obtained in Y_2O_3 has not been found, although we predict finding the same trend in the electron-phonon coupling strength for other host lattices.⁷

To explain the observed trend of the electron-phonon coupling strength $\bar{\alpha}$ qualitatively, we suggest the following two parameters: (a) lanthanide contraction and (b) shielding of the $4f$ electrons.

(a) Due to the lanthanide contraction the average electron-nucleus distance $\langle r^2 \rangle_{4f^n}$ will decrease through the series.⁴¹ Since this will cause a decrease of the overlap of the $4f$ orbitals with the orbitals of the ligands, it is supposed that the lanthanide contraction induces a decrease of the electron-phonon coupling strength through the lanthanide-ion series.

(b) The shielding parameter σ_2 describes the shielding or screening of the $4f$ electrons by the $5s$ and $5p$ electrons.^{42,43} The most complete overview of shielding parameters of trivalent lanthanide ions is given by Blok and Shirley.⁴⁴ According to their data, there is a gradual decrease of the shielding from Ce^{3+} ($\sigma_2=1.1$) to Yb^{3+} ($\sigma_2=0.6$). This means that the $4f$ electrons in the beginning of the lanthanide-ion series are better screened from the crystal field than the $4f$ electrons at the end of the series: this implies an increase of

the electron-phonon coupling strength through the series. The lanthanide contraction on the one hand, and the shielding of the $4f$ electrons on the other hand might result in this symmetric behavior of the electron-phonon coupling strength, since they have opposite effect.

The data given by Blok and Shirley are not uncontroversial. Newman and Price⁴⁵ suggest a much higher shielding for Gd^{3+} ($\sigma_2=0.9$, instead of 0.61). Others^{46,47} have calculated σ_2 parameters of Pr^{3+} and Tm^{3+} differently from those given by Blok and Shirley, but both Refs. 46 and 47 calculate a higher shielding for the $4f$ electrons of Pr^{3+} than for Tm^{3+} . Fortunately, all these different values for σ_2 fit into our qualitative model that is based on a smaller shielding at the end of the series to explain the increase of the electron-phonon coupling strength beyond Gd^{3+} . A much higher value of the shielding of the $4f$ electrons of Gd^{3+} , suggested in Ref. 45, is also in agreement with the weak electron-phonon coupling of this ion.

Lanthanide contraction and shielding were also used to explain the variation of the vibronic transition probability (A_{vib}) through the lanthanide-ion series.^{7,42} However, to explain the variation of A_{vib} through the series, also the influence of the opposite parity admixing is important.^{5,7,42,49–51} The lower the energy of the opposite parity states, the more these states will be admixed in the $4f^n$ states, which gives an increase in the electron-phonon coupling strength. One might also expect to find an influence of the position of the opposite parity states on the $\bar{\alpha}$ values. At the center of the lanthanide series an influence of the energetic position of the opposite parity states is found indeed: Gd^{3+} has a very weak electron-phonon coupling, Tb^{3+} has a relatively strong coupling, and Eu^{3+} has an intermediate coupling. This behavior reflects the position of the opposite parity states of these ions since these states are situated at relatively high energy for Gd^{3+} ($91\,000\text{ cm}^{-1}$), at very low energy for Tb^{3+} ($54\,900\text{ cm}^{-1}$) and intermediate for Eu^{3+} ($81\,800\text{ cm}^{-1}$).⁵²

To study the variation of the electron-phonon coupling strength for different lanthanide ions in more covalent host lattices, we have performed several line-broadening experiments on trivalent lanthanide ions in La_2O_3 . These experiments show the same variation of the electron-phonon coupling strength through the trivalent lanthanide-ion series: small $\bar{\alpha}$ values were found for Gd^{3+} and larger $\bar{\alpha}$ values for Pr^{3+} , Nd^{3+} , and Er^{3+} .⁵³ However, one has also to take into account that the variation due to the position of the opposite parity states in more covalent lattices will be different from the one in LiYF_4 , since the lowest opposite parity states in the former lattices are often charge-transfer states which have a different variation through the series than the $4f^{n-1}5d^1$ states.^{54,55}

Although the selection rules for the Raman two-phonon process, vibronic transitions and multiphonon relaxation are different, both from line-broadening experiments and vi-

bronic transition probabilities the same symmetric trend in the parameter for the electron-phonon coupling strength ($\bar{\alpha}$ and A_{vib} , respectively) is found when a large number of transitions is considered. This leaves us with the question: why is this variation in the electron-phonon coupling strength not observed in the multiphonon relaxation data, although it is derived from two other manifestations of electron-phonon coupling? This is probably due to the fact that the variation of the electron-phonon coupling strength is not easily found on a logarithmic scale of multiphonon relaxation transition probabilities. Although inclusion of the individual coupling strength is possible, it makes the models for multiphonon relaxation even more complex.

IV. CONCLUSIONS

In conclusion, a variation has been found in the electron-phonon coupling strength through the trivalent lanthanide series. This variation is explained by two effects, lanthanide contraction and the decrease of $4f$ electron shielding, which influence the electron-phonon coupling strength

through the lanthanide series in an opposite way. The result of these effects is a variation of the electron-phonon coupling strength of the trivalent lanthanide-ion series: strong in the beginning and the end of the series and weak in the middle. In the middle of the series also the influence of the position of the $4f^{n-1}5d^1$ states is found: a relatively low position of the $4f^{n-1}5d^1$ states enhances the electron-phonon coupling.

ACKNOWLEDGMENTS

We are grateful to G.J. Dirksen for growing the single crystals. For the measurements on $\text{LiYF}_4:\text{Ce}^{3+}$ we thank Professor Dr. J. H. van der Maas, Dr. E. Th. G. Lutz, and E. van der Windt of the Utrecht University. For the measurements on $\text{LiYF}_4:\text{Yb}^{3+}$ we are grateful to Professor Dr. H. U. Güdel and T. Riedener of the University of Bern, Switzerland. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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- ${}^6I_{7/2} \Rightarrow {}^8S_{7/2}$ transitions. Correction has been performed for the difference in refraction index (YOCl $n_{310\text{ nm}}=1.6$; LiYF₄ $n_{310\text{ nm}}=1.488$).
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