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Spectral-line-broadening study of the trivalent lanthanide-ion series. I. Line broadening as a probe of the electron-phonon coupling strength

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Line broadening is evaluated as a method to probe an electron-phonon coupling strength of lanthanide ions. Various problems which complicate the analysis of line broadening, like a contribution of different relaxation processes and the difference in behavior for different transitions in the same system are discussed, using $LiYF_4$:Eu^{3+} and $LiYF_4$:Pr^{3+} as examples. The results show that the electron-phonon coupling parameter $\overline{\alpha}$, derived from a fit to the Raman two-phonon process for different transitions, provides a good estimate of an electron-phonon coupling strength. In a second paper this line-broadening method is used to probe the variation of the electron-phonon coupling strength through the trivalent lanthanide-ion series. [S0163-1829(97)00101-X]

I. INTRODUCTION

The electron-phonon coupling of trivalent lanthanide ions has been a subject of study for several decades. Not only from a fundamental point of view is there interest in this subject, but also from an applied one. In the application of lanthanide ions in, for example, laser materials, fiber amplifiers for telecommunication, or luminescent materials, electron-phonon coupling can play an important role. The electron-phonon coupling manifests itself in several ways; viz. multiphonon relaxation, vibronic sidebands, and line broadening, and line shift with increasing temperature.[1,2]

Part of the research in our group is concentrated on this electron-phonon coupling. We are especially interested in the answer to the question whether there is a trend in the electron-phonon coupling strength through the trivalent lanthanide ion series. The reason for this interest is that although phenomena like multiphonon relaxation,[3] vibronic sidebands,[4] and line broadening[5,6] have been studied thoroughly for many individual trivalent lanthanide ions, the reports on a systematic *variation* of the electron-phonon coupling strength through the lanthanide series are rather scarce.[7–9] This lack of knowledge is the motivation of our research of the electron-phonon coupling strength of lanthanide ions in several host lattices like $LiYF_4$ and La_2O_3.

In the past, the research in our group on the electron-phonon coupling strength was concentrated on the vibronic transitions of $Pr^{3+}(4f^2)$, $Gd^{3+}(4f^7)$, and recently also $Tm^{3+}(4f^{12})$.[4,10–13] The vibronic transition probabilities (A_{vib}) of several transitions of these ions were obtained and compared for several host lattices. The results of this work on the vibronic transition probabilities, seem to indicate that the electron-phonon coupling strength is large in the beginning and the end of the series, but small in the middle. This behavior of the electron-phonon coupling strength can be explained by considering the energetic position of the opposite parity states, the lanthanide contraction and the shielding of the $4f$ electrons by the $5s^2$ and $5p^6$ electrons.

However, as shown in Ref. 13, the vibronic transition probabilities are in some cases hard to obtain. To obtain more evidence whether or not there is a variation in the electron-phonon coupling strength, we have chosen another way to evaluate the electron-phonon coupling strength for different lanthanide ions. In this series of two papers we report linewidth measurements as a function of temperature on several transitions of nine trivalent lanthanide ions (Ce^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+}) in $LiYF_4$. In comparison to the measurements of the vibronic transition probabilities, the linewidth measurements are a relatively easy method to evaluate an electron-phonon coupling strength of lanthanide ions.

In the past, many linewidth broadening studies have been performed on lanthanide ions and transition-metal ions in various crystalline systems. Examples are given in Refs. 5, 6, and 14–21. The aim of most of those studies was to elucidate the mechanism responsible for the line broadening. In this first paper the method of temperature-dependent line broadening to study the variation of an electron-phonon coupling strength is evaluated. Several problems will be discussed: (A) the influence of the choice of the Debye temperature on the electron-phonon coupling parameters, (B) the importance of the contributions to the total linewidth of the direct process and the Raman process, and (C) the variation of electron-phonon coupling parameters for different transitions of *one* lanthanide ion. These problems are discussed using the line broadening for several transitions of Eu^{3+} and Pr^{3+} in the host lattice $LiYF_4$ as examples. It is shown that line broadening is a reliable and relatively easy method to study an electron-phonon coupling strength through the trivalent lanthanide ion series.

In the subsequent paper (part II) an overview of the line-broadening results of nine lanthanide ions is given. In that paper the variation in the electron-phonon coupling strength as derived from line-broadening experiments is dealt with. Also parameters that can qualitatively explain the variation are suggested.

II. THEORY

The summary of the theory on linewidth broadening given below, is mainly derived from Refs. 1, 2, 5, and 6. The linewidth of a zero-phonon line is determined by the lifetime of the starting and final level. The total linewidth $[\Delta E(T)]$

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depends on the temperature (T) and is a summation of several contributions. $\Delta E(T)$ is given by

$$\Delta E(T) = E^{\mathrm{Inh}} + E^{D}(T) + E^{R}(T) + E^{\mathrm{Orb}}(T) + E^{\mathrm{MR}}(T) + E^{\mathrm{Rad}}. \tag{1}$$

In this equation most of the possible contributions to the linewidth are given; in reality however, only a few of them contribute significantly. The contributions in Eq. (1) are due to the inhomogeneous broadening (E^{Inh}), the direct process (or one-phonon process, E^{D}), the Raman (two-phonon) process (E^{R}), the Orbach (two-phonon) process (E^{Orb}), multiphonon relaxation (E^{MR}), and radiative relaxation (E^{Rad}), respectively. These different contributions will be explained below.

The inhomogeneous contribution to the linewidth is due to random crystal-strain inhomogeneities. This temperature-independent contribution gives a Gaussian line shape and depends on the disorder in the host lattice. Typically, at 4.2 K the inhomogeneous linewidth for transitions of lanthanide ions varies from 0.1 cm^{-1} in a high-quality single crystal to some 100 cm^{-1} in a glass.[5,6,22,23]

$E^{D}(T)$ is the contribution due to the direct or one-phonon process: one phonon is emitted or absorbed. This contribution is described by

$$E^{D}(T) = E^{D}_{\mathrm{em}}(T) + E^{D}_{\mathrm{abs}}(T) = \sum_{j<i} \beta_{ij}(n+1) + \sum_{j>i} \beta_{ij}(n). \tag{2}$$

In this equation, n is the phonon occupation number $[\exp(\Delta E_{ij}/kT) - 1]^{-1}$, and i and j are two levels, for example, crystal-field components of one term, at a distance ΔE_{ij} from each other. The energy difference ΔE_{ij} is within the range of phonon energies of the system. β_{ij} is the electron-phonon coupling coefficient for the direct process. The direct process gives a Lorentzian line shape. From the formula it can be derived that at low temperatures the contribution of one-phonon absorption vanishes, whereas the contribution of the one-phonon emission does not $(\Sigma_{j<i}\beta_{ij})$.

Next to the one-phonon process, two-phonon relaxation processes also exist: the Raman two-phonon process $[E^{R}(T)]$ and the Orbach two-phonon process $[E^{\mathrm{Orb}}(T)]$. In the Raman two-phonon relaxation, a certain level i absorbs a phonon that bridges the gap to an intermediate level j'; the system relaxes with a higher energetic phonon to level j. The Raman two-phonon process is a nonresonant process, and the energy differences $\Delta E_{ij'}$ and $\Delta E_{j'j}$ are assumed to be much larger than the range of phonon energies in the system. There is also an intrinsic Raman two-phonon process: the phonons that are absorbed and emitted are of the same energy.[1]

Using the Debye approximation of phonon energies, it can be derived that the temperature-dependent contribution to the linewidth by the Raman process is described by

$$E^{R}(T) = \overline{\alpha}\left(\frac{T}{T_D}\right)^{7} \int_{0}^{T_D/T} \frac{x^{6}e^{x}}{(e^{x}-1)^{2}}\, dx. \tag{3}$$

In this equation $\overline{\alpha}$ is the electron-phonon coupling parameter for the Raman process, T_D is the effective Debye temperature and $x = \hbar\omega/kT$. In the Debye approximation the density of phonon states $\rho(\omega)$ scales with ω^{2}, the square of the phonon frequency. Although the Debye model is rather rough, in practice the thermal behavior of the linewidth is described quite well by a single characteristic temperature. This effective Debye temperature T_D can differ from the one derived from the phonon cutoff energy (ω_D) or calculated from, e.g., specific-heat data (see Sec. IV A).[24]

The contribution of the Orbach process arises from a resonant two-phonon process: the energy differences between levels i, j, and j' are *within* the range of phonon energies of the system. In most linewidth studies the contribution of the Orbach process is neglected. It is supposed to be only effective in the case of relaxation between the Zeeman split levels of a Kramers ion; in that case the contribution of the direct and Raman process are of minor importance.[1,25,26]

Multiphonon relaxation, the simultaneous emission of more than one phonon to bridge the energy difference to a lower lying level, enters Eq. (1) via $E^{\mathrm{MR}}(T)$. The contribution of this process is also assumed to be negligible in most cases.[6]

The last term, E^{Rad} is the contribution due to the radiative relaxation of a state. Since the radiative relaxation times of intra $4f^{n}$ transitions of trivalent lanthanide ions are of the order of some μs to ms, this contribution can be neglected. Lifetimes like these give, according to the Heisenberg principle, contributions of less than 5×10^{-6} cm^{-1} to the total width.[6]

Since the contributions to the total linewidth of the Orbach process, multiphonon relaxation and the radiative relaxation can be neglected, the formula for the total linewidth contains only the contributions from the inhomogeneous linewidth, the direct process and the Raman two-phonon process. Many papers neglect also the direct process (see, for example, Refs. 5, 16, 21, and 27). Its contribution can be relatively large at lower temperatures, but at higher temperatures the Raman process becomes dominant. When the direct process is neglected, Eq. (1) simplifies to

$$\Delta E(T) = E^{\mathrm{Inh}} + E^{R}(T) = E^{\mathrm{Inh}} + \overline{\alpha}\left(\frac{T}{T_D}\right)^{7} \int_{0}^{T_D/T} \frac{x^{6}e^{x}}{(e^{x}-1)^{2}}\, dx. \tag{4}$$

Although this simplification will introduce an error in the fit values (T_D and $\overline{\alpha}$), it seems satisfying in many cases. In Sec. IV it will be shown that Eq. (4) is also appropriate in this study.

III. EXPERIMENT

A single crystal of $\mathrm{LiYF_4}$ with $\mathrm{Pr^{3+}}$ as dopant ion was grown using the Bridgman method. The crystal growth melt contained 0.05 mole % of dopant ion. The crystal was transparent and of a good quality. Pieces of some 1.5 mm thick were used for the measurements. A crystalline powder of $\mathrm{LiYF_4}$ with dopant $\mathrm{Eu^{3+}}$ was prepared according to the procedure described in Ref. 28. The samples were checked by x-ray powder-diffraction analysis and found to be single phase. $\mathrm{LiYF_4}$ has the inverse scheelite structure, space group $I4_1/a$. The site symmetry for the lanthanide ion is S_4.[29] Transmission spectroscopy showed that the samples did not contain optical impurities.

High-resolution measurements were carried out using an excimer-laser-pumped dye laser setup. The excimer laser setup consists of a Lambda Physik LPD3002 tunable dye laser which is pumped by a Lambda Physik LPX100 excimer (XeCl) laser. The typical linewidth of the dye laser output is 0.18 cm^{-1}. The sample is mounted in an Oxford Instruments liquid-helium bath cryostat. Emission spectra were recorded with a 1 m focal length Spex 1704 monochromator with a resolution of some 0.2 cm^{-1}. The temperature of the samples in the cryostat could be varied between 2 K and room temperature. Above room temperature use was made of a home-made high-temperature cell (see Ref. 30).

The linewidths of the transitions were either derived by fitting the line shape, or from the spectra (width at half height).

IV. RESULTS AND DISCUSSION

In this section three important aspects of the line broadening for lanthanide ions will be discussed, using results for Eu^{3+} and Pr^{3+} in LiYF_4 as examples. First the choice of the Debye temperature (T_D) is dealt with (Sec. IV A), and second, the contribution of the direct process to the linewidth (next to the dominant Raman process) is discussed (Sec. IV B). Finally, the variation of the line broadening as a function of temperature for different transitions on the same ion in the same host lattice will be discussed (Sec. IV C).

A. The Debye temperature (T_D)

The theoretical models for the temperature-dependent line broadening by Raman two-phonon relaxation processes, assume a Debye distribution of the phonon density of states, i.e., $\rho(\omega)$ scales with ω^2. Above the phonon cutoff frequency (ω_D) the density of states drops to zero. This phonon cutoff frequency is related to the Debye temperature via $T_D=\hbar\omega_D/k$. The assumption of a Debye distribution of the phonon density of states is necessary to derive the analytical expression for the Raman two-phonon process [Eq. (3)]. In practice, however, it is found that a Debye temperature that is lower than the Debye temperature determined from the phonon cutoff frequency, gives a better fit of the experimentally observed temperature dependence of the linewidth to Eq. (3), see also Refs. 5, 16, and 24. The fact that a lower Debye temperature gives a better fit can be explained by the fact that the real density of phonon states does not fit the Debye model exactly: the density of phonon states for lower energetic phonons is considerably higher than predicted in the Debye model. In the case of LiYF_4 an extra argument for the choice of a lower Debye temperature will play a role. Since the lanthanide ion substitutes for the Y^{3+} ion, the main ion-phonon interaction will involve vibrations with the F^- ligands. These are relatively lower in energy than the Li-F vibrations which determine the phonon cutoff frequency.[31]

An effective Debye temperature can, for example, be estimated from elastic constants, the distribution of the phonon density of states (from neutron-diffraction data or vibronic sidebands) or from the Debye temperature that gives the best fit to the experimental data. In the literature the value of T_D for LiYF_4, based on elastic constants of the crystal is 403 K.[32] The value that can be derived from the phonon cutoff frequency (570 cm^{-1}, Refs. 31 and 33) is 780 K. We have chosen to derive the value of T_D from fits to the experimental data. In Table I, an example is shown of fits to the linewidth of the ${}^5D_0(\Gamma_1)\Rightarrow{}^7F_2(\Gamma_{3,4})$ transition of LiYF_4:Eu^{3+} with six different Debye temperatures (T_D=150, 200, 250, 300, 400, and 500 K). It is clear that $\overline{\alpha}$ increases when a higher T_D is chosen. With decreasing Debye temperature the error decreases also, although temperatures below 250 K do not improve the fits considerably. Since the choice of a T_D of 200 K (or lower) would give an unrealistic Debye temperature in view of the data from the literature, we have chosen for T_D=250 K. Also for other transitions this relatively low value of T_D gives a good fit of the experimentally observed temperature dependence of the linewidth. The choice of 250 K for T_D is somewhat arbitrary, but in this comparative study the exact value of T_D is not of major importance since another choice of T_D would change the absolute $\overline{\alpha}$ values, but not their relation.

TABLE I. $\overline{\alpha}$ values for different Debye temperatures. The error is defined as $\sigma=\Sigma_i|\text{ fit value }_i-y_i|/\Sigma_i y_i$.

T_D (K)	$\overline{\alpha}$ (cm^{-1})	σ
150	4.4	0.066
200	7.9	0.067
250	13	0.068
300	19	0.069
400	35	0.073
500	60	0.077

By using the same value of T_D for LiYF_4 for all fits, the $\overline{\alpha}$ values for different transitions of different lanthanide ions can be compared. Therefore, a possible variation in an electron-phonon coupling strength of trivalent lanthanide ions can be derived from the variation of the Raman two-phonon coefficient $\overline{\alpha}$.

B. The contribution of the direct process

The general expression for the temperature-dependent line broadening [Eq. (1)] contains several contributions. As discussed in Sec. II, the two important temperature-dependent phonon relaxation processes that contribute to the line broadening are the Raman two-phonon process and the one-phonon absorption and emission processes (direct process). In many papers the direct process is neglected, although it has been shown several times, that the contribution of one-phonon relaxation processes to the linewidth can be significant.[6,14,19,20,34] The evaluation of the contribution of the direct process to the total linewidth is not an easy task, since one has to take into account one-phonon emissions and absorptions to a number of crystal-field components of the starting and final levels. Especially when many crystal-field components are present, the calculation of the unknown β parameters can be quite difficult.[20] Only for transitions where a few closely spaced crystal-field components are involved in the direct process, the evaluation of the β parameters can be straightforward. Otherwise, one has either to take into account only a limited number of all the (by one phonon) accessible levels,[6,19,20] or, as is done in Ref. 14, one has to assume that the β's scale with the cube of the resonant phonon energy ($\beta\sim\omega^3$).

Thus, there are two approximations: one considering only the Raman process and one considering both the direct and

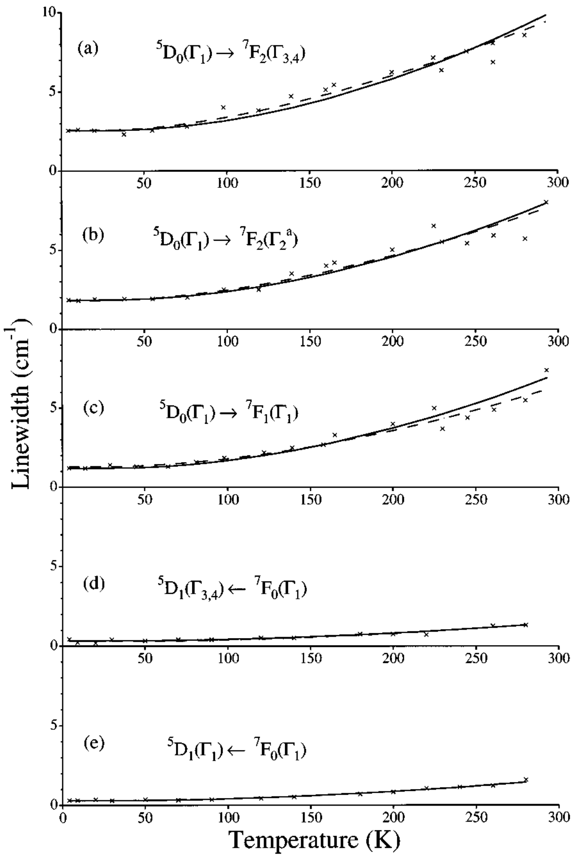

FIG. 1. Fits and simulations to the temperature-dependent linewidths of LiYF$_4$:Eu^{3+}. (a) $^5D_0(\Gamma_1)\Rightarrow{}^7F_2(\Gamma_{3,4})$; (b) $^5D_0(\Gamma_1)\Rightarrow{}^7F_2(\Gamma_2^g)$; (c) $^5D_0(\Gamma_1)\Rightarrow{}^7F_1(\Gamma_1)$; (d) $^5D_1(\Gamma_{3,4})\Leftarrow{}^7F_0(\Gamma_1)$; (e) $^5D_1(\Gamma_1)\Leftarrow{}^7F_0(\Gamma_1)$. The full lines are the fits according to the Raman process only [Eq. (4)]; the dashed lines are the fits/simulations including both Raman and direct processes.

the Raman process as temperature-dependent line-broadening mechanisms. In this study the contribution of the direct process to the total linewidth is evaluated for several transition on Eu^{3+} and Pr^{3+} in LiYF$_4$. The assignment and position of the energy levels of LiYF$_4$:Eu^{3+} are derived from Ref. 35, and of LiYF$_4$:Pr^{3+} from Ref. 36.

1. *LiYF$_4$:Eu^{3+}*

For Eu^{3+} the temperature dependence of the line broadening was studied for five transitions. The linewidth data are shown in Figs. 1(a)–1(e). These data were fitted with only the Raman process as a temperature-dependent line-broadening contribution, according to Eq. (4) (full line), and simulated including both the direct and the Raman processes (dashed line).

Fits to the Raman process. The parameters of the fits without the direct process are found in Table II, column 4: the $\overline{\alpha}$ values are found as the coefficients of the term $E^R(T)$ [see Eq. (3)]; the values for E^{Inh} are the experimental linewidths at 4.2 K (see Fig. 1); both values depend on the transition studied.

Simulations including both direct and Raman process. The parameters for the simulations including both the direct (one-phonon) and the Raman (two-phonon) processes are found in Table II column 2. The levels which are accessible by one phonon from either the starting or the final levels, are included in the simulations. The energy differences between the levels between which one-phonon processes play a role, are derived from Ref. 35. These energy differences are indicated in Table II, column 2 as numbers between parentheses. The $\overline{\alpha}$ values of these fits/simulations including both the direct and the Raman process are found as the coefficients of the term $E^R(T)$ in Table II, column 2.

The first value that will be evaluated is the inhomogeneous linewidth. Following Yen, Scott, and Schawlow,[6] we suppose that the inhomogeneous linewidth is the same for all transitions. This assumption is not necessarily true, but it introduces only a relatively small error. From the transitions with the smallest linewidth at 4.2 K, the $^5D_1\Leftarrow{}^7F_0$ transitions, we have estimated E^{Inh} to be 0.3 cm^{-1}.

The next values that have to be evaluated are the β's, the electron-phonon coupling parameters for the direct process. The procedure to derive these parameters is the same as applied in Refs. 6, 19, 20, and 34: from the linewidths at 4.2 K and the temperature-dependent linewidths these β's can be calculated. Since not all β parameters can be calculated from the linewidth data at 4.2 K, the unknown β parameters have to be included in the fit. Due to the large number of fitting parameters (the β parameters and $\overline{\alpha}$), fitting can become im-

TABLE II. Fits of the transitions studied for LiYF$_4$:Eu^{3+} including the direct process (column 2), and omitting the direct process (column 4). The assignment of the transitions and the energy differences ({number}) between the levels involved in the direct processes are derived from Ref. 35. $n=[\exp(\Delta E_{ij}/kT)-1]^{-1}$, n stands for the one-phonon absorption; $(n+1)$ for the one-phonon emission, {number} $=$the difference in energy (ΔE_{ij}) between the two levels between which the direct process occurs, $E^R(T)=$the formula for the Raman process, its coefficient is $\overline{\alpha}$ [see Eq. (3)].

Transition	Fit equation, including the direct and the Raman processes	σ	Fit equation including only the Raman process	σ
$^5D_1(\Gamma_1)\Leftarrow{}^7F_0(\Gamma_1)$	$0.3+0.5\{334\}n+0.5\{430\}n+4.1E^R(T)$	0.05	$0.3+4.8E^R(T)$	0.06
$^5D_1(\Gamma_{3,4})\Leftarrow{}^7F_0(\Gamma_1)$	$0.3+0.5\{334\}n+0.5\{430\}n+3.6E^R(T)$	0.12	$0.3+4.2E^R(T)$	0.11
$^5D_0(\Gamma_1)\Rightarrow{}^7F_1(\Gamma_1)$	$0.3+0.5\{96\}(n+1)+0.5\{(n+1)+0.5\{461\}n+15E^R(T)$	0.09	$1.2+17.2E^R(T)$	0.11
$^5D_0(\Gamma_1)\Rightarrow{}^7F_2(\Gamma_2^g)$	$0.3+0.5\{461\}(n+1)+1\{557\}(n+1)+0.7\{85\}n+1.5\{259\}n+14E^R(T)$	0.10	$1.8+23E^R(T)$	0.10
$^5D_0(\Gamma_1)\Rightarrow{}^7F_2(\Gamma_{3,4})$	$0.3+1.5\{546\}(n+1)+0.7\{85\}(n+1)+1.4\{174\}n+1.4\{196\}n+13E^R(T)$	0.07	$2.6+27E^R(T)$	0.08

possible. Therefore, we have performed simulations of the linewidth data in the case where we could not achieve reliable fit data. Although the error in the β values might now become large (some 50%), there is not much freedom to change them too much, since the linewidth data at 4.2 K do not permit this. Consider the following example: the homogeneous linewidth of the $^5D_0(\Gamma_0)\Rightarrow{}^7F_2(\Gamma_2^a)$ transition at 4.2 K is 1.5 cm^{-1}. Although the exact β values belonging to the one-phonon emissions from level $^7F_2(\Gamma_2^a)$ might differ from the found fit values, $E^{\mathrm{Inh}}+\Sigma_{j<i}\beta_{ij}$ (in which $i=\Gamma_2^a$) must be 1.5 cm^{-1}. This means that, although we do not know the β values exactly, we can derive from the spectra at the 4.2 K limit values for these β's.

Comparison of the two approximations. By including the direct process, the error becomes smaller and the linewidth data are described better than including the Raman process only. This can also be seen from Figs. 1(a)–1(e), although in some cases the two lines are similar.

It is clear from Table II that by including the direct process, the $\bar{\alpha}$ values can be up to 50% smaller. With Gourley[19] we conclude that neglecting the direct process introduces a considerable error in the $\bar{\alpha}$ value. This error in the $\bar{\alpha}$ value will be larger when more levels accessible by one phonon are nearby. However, another conclusion from Table II is that, although by incorporation of the direct process the $\bar{\alpha}$ values change, the same order of magnitude of the electron-phonon coupling strength is still found. This seems to imply that if we want to compare different transitions, or even different transitions of different lanthanide ions, we do, in most cases, not need to take into account the contribution of the direct process.

2. *LiYF$_4$:Pr^{3+}*

To support the conclusion from the previous section, some linewidth measurements have been performed on a system with an early lanthanide ion: LiYF$_4$:Pr^{3+}. Six transitions were studied of which six were fitted to the Raman process only, and three were simulated including both the Raman and the direct processes. The data and fits/simulations are shown in Figs. 2(a)–2(f) and in Table III. The procedure followed was the same as for LiYF$_4$:Eu^{3+}.

From Table III it can be derived that the direct process has a significant contribution to the total linewidth, even more than in the case of Eu^{3+}. The reason for this is most probably that the levels that are involved in the studied transitions have a large number of crystal-field components ($^3H_6$,$^3H_4$). Although the direct process has a significant contribution, it is clear that the Raman process is still dominant. This is in line with the observations for LaF$_3$:Pr^{3+} (Ref. 6). Another conclusion from Table III is that with or without including the direct process, the $\bar{\alpha}$ values change but the same order of magnitude of the electron-phonon coupling strength is found. This was also the case for Eu^{3+}. This confirms the conclusion (of Sec. IV B 1) that if we want to compare different transitions, or different transitions of different lanthanide ions, we do not need to take into account the contribution of the direct process.

C. Variation of the $\bar{\alpha}$ values of one ion

The results in Tables II and III show that the $\bar{\alpha}$ values derived from the temperature dependence of the linewidths vary considerably for different transitions on one ion. For the five transitions studied for Eu^{3+} the $\bar{\alpha}$ values range from 4.2 to 27 cm^{-1}, and for the transitions on Pr^{3+} from 30 to 161 cm^{-1}. This large variation of $\bar{\alpha}$ values for different transitions is in agreement with previous observations. For example, it has also been found for the systems YAG:Nd^{3+} (Ref. 5), LaF$_3$:Pr^{3+} (Ref. 6), and Al$_2$O$_3$:Cr^{3+} (Ref. 14). This variation of $\bar{\alpha}$ values can be ascribed to a difference in electron-phonon coupling strength for the different levels. The results in Table II show that for Eu^{3+} the $^7F_1$ and $^7F_2$ levels have a relatively strong coupling (resulting in large $\bar{\alpha}$ values for transitions involving one of these levels), while the $^5D_0$, $^5D_1$, and $^7F_0$ levels have a weaker coupling. Since there is such a large variation of $\bar{\alpha}$ values for different transitions on the same ion, it is important to measure a large number of transitions for one ion to get an idea of the range of $\bar{\alpha}$ parameters. By comparing the range of $\bar{\alpha}$ parameters for different lanthanide ions, one can compare the electron-phonon coupling strengths of different ions. For example, comparison of our results on the $\bar{\alpha}$ values of Pr^{3+} (ranging from 30 to 161 cm^{-1}) and Eu^{3+} (ranging from 4.2 to 27 cm^{-1}) shows that the electron-phonon coupling for the Raman two-phonon process for Eu^{3+} is weaker than for Pr^{3+}.

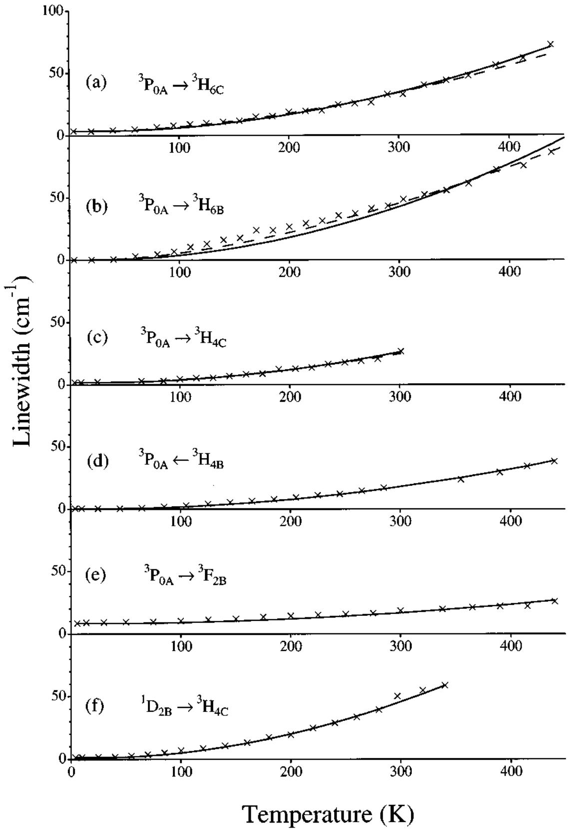

FIG. 2. Fits and simulations to the temperature-dependent linewidths of LiYF$_4$:Pr^{3+}. (a) $^3P_{0A}\Rightarrow{}^3H_{6C}$; (b) $^3P_{0A}\Rightarrow{}^3H_{6B}$; (c) $^3P_{0A}\Rightarrow{}^3H_{4C}$; (d) $^3P_{0A}\Leftarrow{}^3H_{4B}$; (e) $^3P_{0A}\Rightarrow{}^3F_{2B}$; (f) $^1D_{2B}\Rightarrow{}^3H_{4C}$. The full lines are the fits according to the Raman process only [Eq. (4)]; the dashed lines are the fits/simulations including both Raman and direct processes. (d)–(f) are only fitted to Eq. (4).

V. CONCLUSIONS

In this paper the line broadening for transitions within the $4f^n$ configuration of trivalent lanthanide ions is evaluated as

TABLE III. Fits of the transitions studied for $LiYF_4$:Pr^{3+} including the direct process (column 2), and without the direct process (column 4). The assignment of the transitions and the energy differences ({number}) between the levels involved in the direct processes are derived from Ref. 36.

Transition	Fit equation, including the direct and the Raman processes	σ	Fit equation including only the Raman process	σ
$^3P_{0A}\Rightarrow{}^3H_{6B}$	$0.25+3.25\{81\}n+5\{140\}n+8\{161\}n+9\{249\}+82E^R(T)$	0.07	$0.25+153E^R(T)$	0.15
$^3P_{0A}\Rightarrow{}^3H_{6C}$	$0.25+3.25\{81\}(n+1)+0.05\{59\}n+0.7\{80\}n+3\{168\}n+73E^R(T)$	0.07	$3.5+111E^R(T)$	0.05
$^3P_{0A}\Rightarrow{}^3H_{4C}$	$0.25+1.5\{79\}(n+1)+0.2\{134\}n+2\{412\}n+69E^R(T)$	0.05	$1.85+88E^R(T)$	0.05
$^3P_{0A}\Leftarrow{}^3H_{4B}$			$0.3+63E^R(T)$	0.06
$^1D_{2B}\Rightarrow{}^3H_{4C}$			$1.3+161E^R(T)$	0.06
$^3P_{0A}\Rightarrow{}^3F_{2B}$			$8.3+30E^R(T)$	0.09

a method to study the electron-phonon coupling strength. Some transitions on $LiYF_4$:Eu^{3+} and $LiYF_4$:Pr^{3+} were studied as examples.

The results show that the temperature-dependent line broadening can, in good approximation, be described by including only the Raman two-phonon process as the dephasing mechanism. The direct (one-phonon) process contributes as well: however, it is not necessary to include it for a comparative study of the electron-phonon coupling strength.

The choice of the Debye temperature (T_D) for the Raman two-phonon process is somewhat arbitrary. Reliable fits were obtained for a T_D of 250 K for $LiYF_4$, which is lower than the T_D derived from the phonon cutoff energy of 570 cm^{-1}.

The values found for the electron-phonon coupling parameter $\overline{\alpha}$ (from fits to the Raman two-phonon process) vary for different transitions on the same ion. To compare electron-phonon coupling strength for different ions, a large number of transitions has to be measured to obtain a range of $\overline{\alpha}$ values. Summarizing, it is shown that temperature-dependent linewidth measurements provide a feasible method to study the relative electron-phonon coupling strength for lanthanide ions.

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