High-pressure studies on configuration interactions of Pr^{3+} in different hosts

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High-pressure data of the energy levels of Pr^{3+} in $LaCl_3$ and LaOCl are used for the determination of free-ion and crystal field parameters under pressure. In addition to the conventional calculation considering only the $4f^2$ configuration, the excited configurations $4f^15d^1$ and $4f^16p^1$ under pressure are now taken into account. The inclusion of the excited configurations requires many new parameters. In order to limit the number of parameters that have to be varied under pressure, VUV excitation spectroscopy has been employed. From these measurements, the position as well as the shift of the $4f^15d^1$ configuration is determined as a function of pressure. The effect of the excited configurations on the free-ion parameters is found to be negligible. However, the conventional crystal-field parameters $B_q^k(f,f)$, acting within the ground $4f^2$ configuration, show distinct changes in their ambient pressure values as well as in their pressure behavior. The difficulties in using crystal-field parameters, derived from parametrizations taking into account only the $4f^2$ configuration, are elucidated with respect to more extended evaluations.

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I. INTRODUCTION

The complex energy level structure of rare-earth ions in crystals serve as a detailed fingerprint for a number of different interactions taking place between the f electrons and the crystal field originating from all constituents of the crystalline environment. The crystal field is usually described within the one-electron approximation by a phenomenological approach. This approach has been quite successful, however, certain difficulties in the calculation of specific ''anomalous'' multiplets, such as, for example, $^2H_{11/2}$ of Nd^{3+} or $^1D_2$ of Pr^{3+}, pointed out that some important part is still missing in the crystal-field parameterization. This problem prompted a large amount of studies dealing with possible extensions of the conventional crystal-field model in order to improve the calculation of the energy levels, especially for the anomalous multiplets.

The most general approach introduces a full parametrization of the anisotropic two-electron interaction. This approach is referred to as the correlation crystal field (CCF).[1] The main problem of the CCF lies in the large number of new parameters increasing the number of conventional crystal-field parameters approximately by a factor of 20. Because it is impossible to determine all these parameters from experimental data, the number of parameters must be reduced by some means. A practical approach with this respect analyzes the various parameters with respect to their influence on the ''anomalous'' multiplets. According to this procedure Li and Reid[2] could identify specific parameters, which were important for the $^2H_{11/2}$ multiplet of Nd^{3+}.

Another, more common way to reduce the number of CCF parameters assumes a certain type of interaction that is mainly responsible for the correlation effects. This leads to special correlations with a smaller number of parameters, as for example the spin- or orbitally correlated crystal field or the δ-function model. A more detailed account of these models has been given for example by Reid and Newman.[1]

Finally, there is also another possibility to improve the description of the crystal-field levels, which extends the basis set of wave functions by the inclusion of excited configurations, without relaxing the one-electron approximation. It has been shown that this approach can greatly improve the description of the energy levels of Pr^{3+}, Nd^{3+}, and U^{3+} in different host crystals by taking into account the excited $4f^{N-1}5d^1$ and $4f^{N-1}6p^1$ configurations.[3,4] A drawback of these studies is, similar to the correlation crystal-field case, the large number of new parameters that are introduced to the energy level calculations. However, many of these new parameters act only within the excited configurations and have negligible influence on the $4f^N$ energy levels. Hence, without serious problems they can be fixed to values derived from Hartree-Fock calculations.

The remaining parameters, which are much more important for the configuration interactions, are the energy differences between the configurations together with the crystal-field and Coulombic parameters linking the respective configurations. Especially the energy differences in connection with high pressure experiments provide an excellent possibility to study configuration interactions in more detail. Under pressure the excited configurations shift to lower energies and thus closer to the $4f^N$ configurations. This should enhance the strength of the interactions.

Numerous high-pressure studies on crystal fields of rare-earth ions can be found in the literature.[5] These include also possible extensions of the conventional crystal-field model, such as the correlation crystal field,[6] the spin-correlated crystal field,[7] and the δ-function model.[8] However, up to now no studies on the explicit inclusion of the excited configurations under pressure have been published. The present work thus analyses previous high-pressure data on $LaCl_3:Pr^{3+}$ and $LaOCl:Pr^{3+}$ with respect to configuration interactions. In addition, some results of VUV measurements in a diamond anvil cell, determining the position of the first excited $4f^15d^1$ configuration, are presented.

II. EXPERIMENTAL

The $LaCl_3$ and LaOCl samples with 1 mol% Pr^{3+} were synthesized in the crystal growth laboratory at the University

Paderborn. $LaCl_3$ crystallizes in the hexagonal UCl_3 structure type with space group $P6_3/m(C_{6h}^2)$. The site symmetry of the La ions is C_{3h}, however, for the crystal-field calculation the effectively equivalent site symmetry D_{3h} is used. LaOCl crystallizes in a tetragonal symmetry with space group $P4/nmm$. The rare-earth ions occupy one site with C_{4v} point symmetry.

The experiments in the VUV region were performed at the experimental station W3.1 (HIGITI) of the synchrotron radiation source HASYLAB (DESY, Hamburg, Germany). The available wavelengths for excitation or absorption experiments range from 30 to 700 nm. A primary monochromator (1 m normal incidence modified Wadsworth monochromator) selects the excitation wavelengths, while the spectral resolution in the high-pressure studies could be adjusted by the exit slit behind the monochromator. An increase in resolution can be achieved by decreasing the exit slit width, which, at the same time, causes lower intensities of the recorded spectra. In order to get reasonable resolutions and intensities, the resolution was set to around 0.1 nm, corresponding to a resolution of 16 cm^{-1} at 40 000 cm^{-1}.

The detection system for the luminescence light consists of either a Spex monochromator with a CCD camera and a cooled photomultiplier for the visible and infrared region, or a Seya-Namioka monochromator with a channel plate detector for the vacuum-ultraviolet region. All excitation spectra taken in the VUV region were detected by recording the $^3P_0(A_1)\rightarrow{}^3H_4(E')4f\text{-}4f$ luminescence transition of the Pr^{3+} ion. A continuous He-flow cryostat allowed to reach temperatures of 8 K with ambient pressure samples and 12 K with the high-pressure cell.

Pressures were generated with a specially adapted small diamond-anvil cell (DAC) with a pressure range up to 35 GPa. To quickly achieve low temperatures, the cell is only 18 mm high with a diameter of 22 mm. The angle between the entrance and exit windows in the cell has been adapted to the 45° angle between the direction of the excitation light and the detection monochromators.

A drilled Inconnel 600 gasket placed between the two diamonds of the DAC forms the sample chamber. The diameter of this chamber is 300 μm with a height of around 80 μm. In the case of $LaCl_3$ the samples consist of single crystals with sizes of around $200\times200\times40$ μm. The orientation of the crystallographic c axis in the high-pressure cell is not known. In the case of LaOCl small pieces of single crystals of the size of around $20\times20\times10$ μm are used to fill the sample chamber. Because the size of the excitation spot is approximately 2000×100 μm, nearly half of the sample chamber can be illuminated.

The pressure was determined from the position of the $^3P_0(A_1)\rightarrow{}^3H_4(E')4f\text{-}4f$ luminescence line in connection with its known pressure-dependent shift.[9] The pressure transmitting medium used was NaCl. Due to the band gap of the diamond windows, measurements under pressure were restricted to energies below 44 000 cm^{-1}.

III. RESULTS AND DISCUSSION

The calculation of the energy levels under pressure utilizes a standard Hamiltonian consisting of a free ion and a crystal-field part (see, for example, Ref. 10). In general, the Hamiltonian used to calculate the energy levels is divided into a free-ion H_{FI} and a crystal-field part H_{CF}:

$$H=H_{\mathrm{FI}}+H_{\mathrm{CF}}.$$

Within the $4f^2$ configuration, the free-ion part can be written as

$$H_{\mathrm{FI}}=\sum_{k=0,2,4,6}F^k+\zeta\sum_{i=1}^{N}s_il_i+\alpha L(L+1)+\beta G(G_2)$$

$$+\gamma G(R_7)+\sum_{k=2,4,6}P^kp_k+\sum_{k=0,2,4}M_km_k.$$

The free-ion interactions can be divided into radial and angular dependent parts. The angular dependence can be calculated exactly, whereas the radial parts are treated as adjustable parameters. Their values are determined via least squares fits of the calculated and experimental energy levels. The most important interactions are the Coulomb interactions, described by the Slater parameters F^k and the spin-orbit coupling, described by the spin-orbit coupling parameter ζ. The parameters α, β, and γ approximate configuration interactions with even parity configurations and the other parameters M_k, P^k represent minor corrections due to further magnetic interactions.

The crystal-field Hamiltonian of the $4f^2$ configuration in the one-electron approximation is usually written as

$$H_{\mathrm{CF}}=\sum_{k,q}B_q^kC_q^{(k)}.$$

Analogous to the free-ion case, this Hamiltonian consists of radial parts, described by crystal-field parameters $B_q^k(f,f)$ and angular parts $C_q^{(k)}(f,f)$, which can be calculated exactly. The allowed values for k and q depend on the site symmetry of the Pr^{3+} ion.

The inclusion of the excited $4f^15d^1$ and $4f^16p^1$ configurations gives rise to additional parameters. For each configuration a set of free ion and crystal-field parameters, acting within the given configuration, must be taken into account. Additionally, configuration interactions are mediated by Coulomb or crystal-field parameters, depending on the type of configurations involved. A summary of all parameters used in the present calculations is given in Table I. To judge on the quality of the overall fits the standard r.m.s. deviation σ is used:

$$\sigma=\left(\sum_i(E_i^{\mathrm{cal}}-E_i^{\mathrm{exp}})^2/(N-P)\right)^{1/2}.$$

E_i^{cal} and E_i^{exp} are the ith calculated and experimental energy levels, respectively, N is the total number of energy levels, and P the number of free parameters used in the fit.

The calculation of σ does not make sense for single multiplets, because N would be smaller than P. In order to assess the quality of the fit in these cases, the mean deviation δ for the crystal-field splittings will be used:

TABLE I. Free-ion and crystal-field parameters for the configurations $4f^2$, $4f^15d^1$, and $4f^16p^1$. Diagonal elements consist of parameters acting within the particular configuration, nondiagonal elements consist of parameters acting between the configurations. For the particular k and q values that occur in the systems studied in this work see Table II.

	$4f^2$	$4f^15d^1$	$4f^16p^1$
$4f^2$	$F^k(f,f,f,f)$, $\zeta(f)$, α, β, γ, M_k, P^k, $B_q^k(f,f)$	$B_q^k(f,d)$	$R^k(f,p,f,p)$, $B_q^k(f,p)$
$4f^15d^1$		$F^k(f,d,f,d)$, $G^k(f,d,d,f)$, $\zeta(d)$, $B_q^k(d,d)$	$B_q^k(d,p)$
$4f^16p^1$			$F^k(f,p,f,p)$, $G^k(f,p,p,f)$, $\zeta(p)$, $B_q^k(p,p)$

$$\delta=\left(\sum_i (\Delta E_i^{\mathrm{cal}}-\Delta E_i^{\mathrm{exp}})^2/N\right)^{1/2},$$

where ΔE_i denotes the crystal-field splitting of the ith level with respect to the particular center of gravity. Another quantity to be used is the crystal-field strength S, which is given according to Ref. 11 by

$$S=\left\{\frac{1}{3}\sum_k \frac{1}{2k+1}\left[B_{k0}^2+2\sum_{q>0}(\mathrm{Re}\,B_{kq}^2+\mathrm{Im}\,B_{kq}^2)\right]\right\}^{1/2}.$$

In a first approximation the crystal-field strength S can be regarded as a direct measure for the size of the crystal-field splittings.

A. Ambient pressure results

The free ion and crystal-field parameters, which are used as starting values for the high-pressure fits, have been determined from the larger experimental data sets at ambient pressure including literature values. In particular, the energy levels for $LaCl_3:Pr^{3+}$ have been taken from Refs. 12 and 13 with the exception of the uncertain $^1I_6$ levels, which were left out. Also the level $^3H_4(3')$ was not considered because of doubts about the ambient pressure assignment arising from the observed pressure shift. For LaOCl:Pr^{3+} the data have been taken from Ref. 9 with some very slight deviations due to new evaluations of excitation measurements.[14] Even with the extensive data sets at ambient pressure, the number of parameters (see Table I) is to large to be determined solely from a fitting of the $4f^2$ energy levels. In particular, it was not possible to unambiguously determine the energy differences to the excited configurations, represented by the free ion parameters F^0, and the configuration interaction parameters $B_q^k(f,d)$, $B_q^k(f,p)$, and $R^k(f,p,f,p)$ at the same time. In the case of LaOCl:Pr^{3+}, for example, a simultaneous fit of $F^0(f,d,f,d)$ and $B_q^k(f,d)$ results in a much too large value of 126 500 cm^{-1} for the onset of the $4f^15d^1$ configuration, compared to the experimental value of 41 600 cm^{-1}. Under pressure the situation is even worse, because the number of experimentally determined energy levels is still lower.

Due to these difficulties, some of the parameters must be determined by different means. A common way to determine parameters, which are connected with the excited configurations, makes use of Hartree-Fock calculations. In many cases these calculations give reasonable values, however, from calculations for the $4f^2$ configuration it is well known that free ion parameters may distinctly deviate from the experimental values. In order to fix at least some of the parameter values connected with the excited configurations, the positions of the $4f^15d^1$ configurations of Pr^{3+} in $LaCl_3$ and LaOCl were determined by means of VUV excitation measurements at the synchrotron radiation source HASYLAB (DESY, Hamburg, Germany). The VUV excitation spectra of the first excited $4f^15d^1$ configurations of $LaCl_3:Pr^{3+}$ and LaOCl:Pr^{3+} are shown in Fig. 1. The onset of the $4f^15d^1$ configurations lies at 47 000 cm^{-1} for $LaCl_3:Pr^{3+}$ and at 41 600 cm^{-1} for LaOCl:Pr^{3+}. As mentioned, in contrast to these experimental results, the fit of the $4f$ levels yielded a value of 126 500 cm^{-1} for LaOCl:Pr^{3+}. This clearly shows that a simple fitting may result in large discrepancies. Therefore, either Hartree-Fock calculations or, preferably, VUV measurements are necessary to get realistic values for the configuration interaction parameters.

Additional parameters that can be checked by a comparison with the experimental data given in Fig. 1, are the free

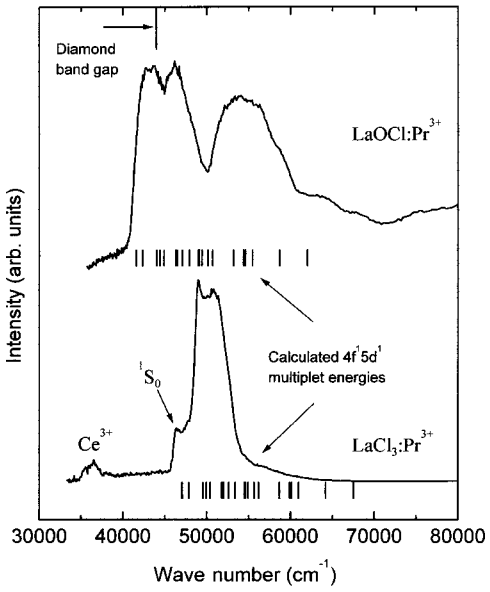

FIG. 1. VUV excitation spectra of $LaCl_3:Pr^{3+}$ and LaOCl:Pr^{3+} at ambient pressure and 6 K. In the $LaCl_3:Pr^{3+}$ spectrum, the line marked with Ce^{3+} most probably originates from a cerium contamination, while the line marked with $^1S_0$ corresponds to the intraconfigurational $^4I_{9/2}\rightarrow{}^1S_0$ transition within the $4f^2$ configuration.

ion parameters of the $4f^15d^1$ configuration. These parameters determine the energies of the multiplets of the excited configuration. With values from Hartree-Fock calculations,[3] the energies of the particular multiplets can be calculated as indicated in Fig. 1 by vertical lines. Obviously, the experimental width of the $4f^15d^1$ configuration is well reproduced by these calculations. Therefore, no significant error is introduced by the use of Hartree-Fock values for the intraconfigurational free ion parameters of the $4f^15d^1$ configuration. This applies for the $4f^15d^1$ configuration itself, as well as for the $4f^2$ energy levels, which are only indirectly influenced by the extent of the excited configurations via slight changes in the energy difference to specific multiplets and thus the mixing of specific $4f^2$ and $4f^15d^1$ energy levels.

The results for the fits taking into account only the $4f^2$ configuration, then $4f^2+4f^15d^1$, and finally $4f^2+4f^15d^1+4f^16p^1$ are shown in Table II. In both cases the $F^0(f,d,f,d)$ parameter was adjusted to reproduce the experimental energy difference between the $4f^2$ and $4f^15d^1$ configurations. Parameters in parenthesis were adopted from Hartree-Fock calculations.[3,4] In all cases the deviation between experimental and calculated energy levels σ is determined almost completely by the uncertainties in the calculation of the crystal-field splittings, which are an order of magnitude larger than the uncertainties of about 0.5 cm^{-1} in the experimental determinations of the line positions.

The successive inclusion of the $4f^15d^1$ and $4f^16p^1$ configurations for $LaCl_3:Pr^{3+}$ results in a decrease of the overall rms deviation from 7.6 to 6.6 cm^{-1} and 5.5 cm^{-1}. However, more interesting is the specific reduction of the deviation of the $^1D_2$ multiplet which especially reveals the problems of the conventional crystal-field calculations. In the present calculations, the mean deviation for the $^1D_2$ multiplet decreases from 18.2 cm^{-1} ($4f^2$ configuration only) to 12.9 cm^{-1} ($4f^2+4f^15d^1$) and finally to 9.5 cm^{-1} ($4f^2+4f^15d^1+4f^16p^1$). Thus, the mean deviation approaches values which can be found also for other multiplets. This selective improvement of the $^1D_2$ multiplet clearly indicates the ability of the configuration interactions to provide significant improvements for the energy level calculations. It should be noted that the size of the improvement due to each of the two configurations is comparable. In the case of LaOCl not only the $^1D_2$ multiplet shows larger deviations, but also the $^3F_4$ multiplet. Their mean deviations when switching on the interaction with the $4f^15d^1$ and finally with the $4f^16p^1$ configuration amount to 23.5, 22.6, and 8.2 cm^{-1} for $^3F_4$ and 21.6, 19.8, and 2.2 cm^{-1} for $^1D_2$. Again these values demonstrate the large improvements due to the configuration interactions. The overall r.m.s deviation decreases from 16.5 to 16.2 cm^{-1} and 10.2 cm^{-1}. This means that the $4f^15d^1$ configuration only slightly improves the calculation of the energy levels of $LaOCl:Pr^{3+}$, whereas the $4f^16p^1$ configuration brings about a very large improvement. Similar observations have been made also in other cases as for example for $LiYF_4:Pr^{3+}$ (Ref. 4) and $YPO_4:Pr^{3+}$.[15]

It is interesting to note that in both systems the crystal field strength *S*, calculated from the crystal-field parameters acting within the $4f^2$ configuration, is distinctly increased when the configuration interactions are taken into account. This points to a general effect of the excited configurations which result in a contraction of the crystal field splittings. Therefore, it must be concluded that the observed splittings of the multiplets do not reflect the real crystal-field strength within the $4f^2$ configuration, but represent an apparently weaker field. The effect of the different model assumptions on the values of the different parameters is clearly illustrated in Table II and later in Fig. 3.

B. High pressure results

In contrast to ambient pressure studies, at high pressure very small samples of the size of 150 μm$\times$150 μm $\times$50 μm have to be used. The small size of the samples often prevents the observation of weak luminescence lines in the diamond-anvil cell. Further difficulties arise with increasing pressure due to a general broadening and in some cases because of an increasing overlap of particular lines. As a result these problems lead to a limited data set under high pressure, compared to ambient pressure measurements.

The limited data set in turn imposes some further restrictions on the number of parameters that can be determined from the experimental data. Actually, within the $4f^2$ configuration only the free-ion parameters $F^k(f,f,f,f)$ for the Coulomb interaction and $\zeta(f)$ for the spin-orbit coupling and the crystal-field parameters $B_q^k(f,f)$ could be varied, while the other parameters had to be fixed under pressure. In the case of the exited configurations all intraconfigurational (F^k,G^k) as well as interconfigurational (R^k) free ion parameters were kept constant. Also the intraconfigurational crystal-field parameters were fixed to zero (this has a negligible influence on the $4f^2$ energy levels[3]).

The remaining parameters are the crystal-field parameters responsible for the configuration interactions and the energy differences between the configurations. As discussed before, it was not possible to simultaneously vary both parameter sets neither at ambient nor at high pressure. Therefore, the crystal-field parameters connected with the excited configurations were treated as free parameters, while high-pressure experiments were used to get the information about the position and the shifts of the excited configurations.

In order to determine the shift of the $4f^15d^1$ configuration under pressure, measurements in a diamond-anvil cell have been performed on $LaOCl:Pr^{3+}$ as shown in Fig. 2. Because the shift of the configuration is determined mainly by a change of the difference of two free ion parameters $F^0(f,d,f,d)$-$F^0(f,f,f,f)$, it can be assumed that the influence of the host on the rate of shift is small and thus the shifts for Pr^{3+} in LaOCl and $LaCl_3$ should be similar. Two observations support this assumption: on the one hand the free ion parameters $F^k(f,f,f,f)$ and $\zeta(f)$ for the two hosts LaOCl and $LaCl_3$ show shifts which deviate by less than 20% up to 8 GPa and on the other hand, the energy difference between $4f^2$ and $4f^15d^1$ at ambient pressure deviates by less than 15% for both hosts. Therefore, also the rate of shift can be expected to deviate by not more than 20%.

According to Fig. 2 the edge of the $4f^15d^1$ configuration shifts by approximately -30 cm^{-1}/GPa. Assuming a negligible change in the intraconfigurational $4f^15d^1$ free ion pa-

TABLE II. Free-ion and crystal-field parameters for $LaCl_3:Pr^{3+}$ and $LaOCl:Pr^{3+}$ at ambient pressure. Values in brackets were kept constant.

	$LaCl_3:Pr^{3+}$			$LaOCl:Pr^{3+}$		
Parameter	$4f^2$	$4f^2+4f^15d^1$	$4f^2+4f^15d^1+4f^16p^1$	$4f^2$	$4f^1+4f^15d^1$	$4f^2+4f^15d^1+4f^16p^1$
$F^0(f,f,f,f)$	11 138	11 237	11 224	11 224	11 305	11 446.8
$F^2(f,f,f,f)$	68 435	68 560	68 525	67 303	67 433	67 417
$F^4(f,f,f,f)$	50 232	50 360	50 378	50 100	50 138	50 231
$F^6(f,f,f,f)$	32 975	33 041	33 066	32 996	32 971	33 018
α	22.8	22.9	22.5	[22.0]	[22.0]	[22.0]
β	−673.4	−669.8	−674.2	[−700]	[−700]	[−700]
γ	1450.9	1422.5	1449.6	[1422]	[1422]	[1422]
M^0	[1.7]	[1.7]	[1.7]	[1.76]	[1.76]	[1.76]
P^2	[266]	[266]	[266]	[275]	[275]	[275]
$\zeta(f)$	745.7	746.6	746.7	742.0	743.5	742.3
$B_0^2(ff)$	106.5	97.8	130.0	−856.8	−963.3	−1225.7
$B_0^4(ff)$	−328.1	−344.2	−347.2	−436.2	−588.6	34.2
$B_4^4(ff)$				945.6	937.2	1222.2
$B_0^6(ff)$	−659.2	−773.9	−798.6	660.2	723.4	643.5
$B_4^6(ff)$				−153.5	−121.2	−388.2
$B_6^6(ff)$	452.2	534.6	510.4			
$F^0(f,d,f,d)$		55 237[a]	55 237[a]		49 890[a]	49 990[a]
$F^2(f,d,f,d)$		[30271]	[30271]		[30271]	[30271]
$F^4(f,d,f,d)$		[15094]	[15094]		[15094]	[15094]
$G^1(f,d,d,f)$		[12903]	[12903]		[12903]	[12903]
$G^3(f,d,d,f)$		[11160]	[11160]		[11160]	[11160]
$G^5(f,d,d,f)$		[8691]	[8691]		[8691]	[8691]
$\zeta(d)$		[1191]	[1191]		[1191]	[1191]
$B_3^3(fd)$		1329	1105			
$B_3^5(fd)$		−5756	−5310			
$B_4^5(fd)$					−6024	−3555
$F^0(f,p,f,p)$			[135237]			[135441]
$F^2(f,p,f,p)$			[11576]			[11576]
$G^2(f,p,p,f)$			[3249]			[3249]
$G^4(f,p,p,f)$			[2973]			[2973]
$R^2(f,f,f,p)$			[−4886]			−3410.1
$R^4(f,f,f,p)$			[−2968]			−1647.2
$\zeta(p)$			[3800]			[3800]
$B_0^2(fp)$			1658			−8355
$B_0^4(fp)$			−5463			−508
$B_4^4(fp)$						13949
$B_3^3(dp)$			[−2965]			
S	162	187	188	367	392	479
N	55	55	55	37	37	37
P	12	14	16	10	11	16
σ	7.4	6.6	5.5	16.5	16.2	10.2

[a]Experimental value.

rameters, this value should be identical with the rate of shift for the whole configuration. However, the signal-to-noise ratio is distinctly worse compared to the ambient pressure spectra in Fig. 1. In addition, due to the band gap of the diamond at around 43 000 cm^{-1} only the onset of the $4f^15d^1$ configuration could be observed. Therefore, the exact value for the rate of shift must be taken with care, although the order of magnitude should be correct.

This result can again be compared with a pure fit of the experimental energy levels with the energy difference between the ground and the excited configuration as a free parameter under pressure. Such a fit for $LaCl_3:Pr^{3+}$ resulted

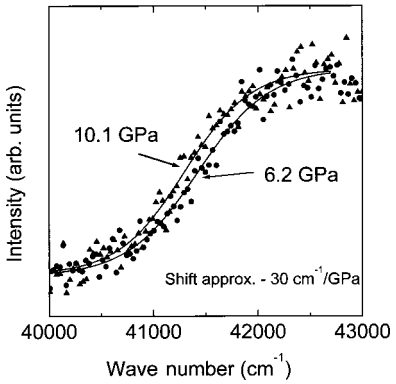

FIG. 2. VUV excitation spectra of the onset of the $4f^2 \rightarrow 4f^15d^1$ transitions for LaOCl:Pr^{3+} at different pressures at 20 K. Circles belong to the spectrum at 6.2 GPa, triangles to the spectrum at 10.1 GPa.

in a redshift of -997 cm^{-1}/GPa for the onset of the excited configuration. Compared to the experimental value and other rates of shift from the literature,[5] the general behavior of a redshift is reproduced, however, the calculated value of nearly -1000 cm^{-1}/GPa is clearly too large. Nevertheless, the result from the pure fit already shows the necessity of increased configuration interactions under pressure to successfully describe the variations of the energy levels.

Taking into account the rate of shift of -30 cm^{-1}/GPa for the $4f^15d^1$ configuration and adopting this value also for the $4f^16p^1$ configuration, the fits of the high-pressure data have been carried out. A rate of shift of -30 cm^{-1}/GPa might underestimate the real shift of the $4f^16p^1$ configuration, however, this can be simply compensated by a stronger change of the interaction parameters. To distinguish the influence of both configurations, in a first step only the $4f^15d^1$ configuration was taken into account and then, in a second step, also the $4f^16p^1$ configuration was added.

The influence of the excited configurations on the pressure variations of the free ion parameters $F^k(f,f,f,f)$ and $\zeta(f)$ was found to be within the experimental errors. Because the same conclusions can thus be drawn about their pressure shifts as discussed in previous works,[10,16] these parameters will not be considered further here.

In contrast to the free ion parameters, the intraconfigurational crystal-field parameters $B_q^k(f,f)$ of the $4f^2$ configuration showed drastic changes when the configuration interaction was introduced. The crystal-field parameters as well as the rms deviation as a function of pressure are shown in Fig. 3.

The conventional fit within the $4f^2$ configuration results in a continuous increase of the r.m.s. deviation for $LaCl_3$:Pr^{3+} from 7.9 cm^{-1} at ambient pressure to 10.3 cm^{-1} at 8 GPa and for LaOCl:Pr^{3+} from 17.5 cm^{-1} at ambient pressure to 19.2 cm^{-1} at 16 GPa. It should be noted that in the case of $LaCl_3$:Pr^{3+} this increase is not due to a worse fitting of the multiplet centroids but solely due to a worse fitting of the crystal-field splittings under pressure. In the case of LaOCl:Pr^{3+} the centroids as well as the crystal-field splittings contribute to the observed increase. In general, this behavior indicates that there is a missing component in the

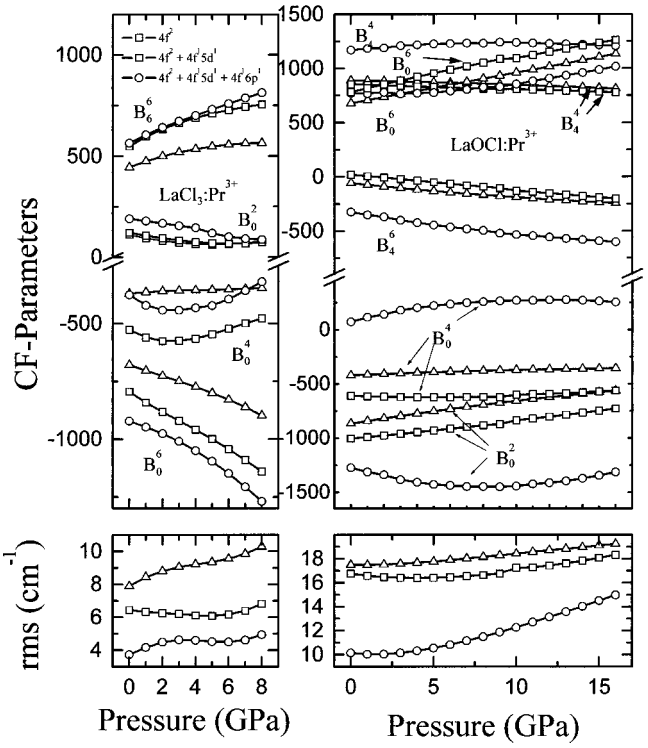

FIG. 3. Crystal-field parameters and the r.m.s. deviation of $LaCl_3$:Pr^{3+} and LaOCl:Pr^{3+} under pressure.

conventional fits which has an increasing influence under pressure. Especially with respect to the $LaCl_3$ results, the missing component seems to belong mainly to the crystal-field part and not to the free ion part. Thus, the additional variation of further free ion parameters would not generally improve the calculation of the energy levels. At the most, only a slight improvement for LaOCl:Pr^{3+} could be expected.

Taking into account the $4f^15d^1$ configuration for $LaCl_3$:Pr^{3+}, however, a distinct improvement of the energy level calculations can be noted. Especially interesting is the fact that the r.m.s. deviation first decreases slightly and then reaches again the ambient pressure value at 7 GPa. Only from 7 GPa to 8 GPa a slight increase of less than 7% is observed. Thus, the strong increase of around 30% for the calculations within the $4f^2$ configuration only, can be completely compensated for by the configuration interactions. In the case of LaOCl:Pr^{3+} the situation is different. Here the general improvement due to the $4f^15d^1$ configuration under pressure is only very small, similar to what has been observed at ambient pressure. Up to 9 GPa no change in the r.m.s. deviation occurs, however, up to the highest pressure achieved in the experiments, the relative increase in the r.m.s. deviation reaches nearly the same value as in the case where only the $4f^2$ configuration has been considered.

A further and even larger improvement of the energy level calculations is achieved when the $4f^16p^1$ configuration is added. However, on the contrary to the fits with only the $4f^15d^1$ configuration, the rms deviation is increasing again under pressure. For $LaCl_3$:Pr^{3+} the increase is less pronounced and mainly occurs from ambient pressure to 2 GPa,

beyond this pressure the deviation is almost constant. Only one further increase from 7 GPa to 8 GPa repeats the behavior already observed in the $4f^15d^1$ fits.

For LaOCl:Pr^{3+} a strong increase of the rms deviation by around 50% removes partly the large improvement obtained at ambient pressure. One reason for this behavior could be that the free ion parameters $R^k(f,p,f,p)$, which mediate a part of the configuration interactions between the $4f^2$ and the $4f^16p^1$ configurations (see Table I), were kept constant under pressure. Unfortunately, due to the low number of experimental energy levels, it is not possible to additionally vary these parameters. Another reason could be that also other excited configurations play a more important role for LaOCl:Pr^{3+}. Therefore, it is not completely clear whether the inclusion of the configuration interactions with the $4f^15d^1$ and $4f^16p^1$ configurations alone could result in a constant r.m.s. deviation for LaOCl:Pr^{3+} under pressure.

As mentioned before, the conventional crystal-field parameters $B_q^k(f,f)$ show pronounced changes when the configuration interactions are introduced. Two effects can be distinguished, on the one hand, a change of the value at ambient pressure and, on the other hand, a change of the pressure behavior. With only a few exceptions all parameters show distinct variations of their ambient pressure values. As discussed in the previous section, this leads to an enhanced value for the crystal-field strength. The characteristics of the pressure behavior, that were observed for $LaCl_3$:Pr^{3+}, can be summarized as follows.

(i) Taking into account the configuration interactions, B_0^6 and B_6^6 still show an increase in their absolute values under pressure. In the case of B_6^6 the increase is slightly larger.

(ii) B_0^4 shows the most distinct changes. When only the $4f^2$ configuration is considered, a very slight decrease of its absolute value is observed, however, in the other cases an increase up to 2 GPa, followed by a strong decrease up to 8 GPa is noted.

(iii) The behavior of B_0^2 changes only slightly when both excited configurations are added. In this case the increase at higher pressures vanishes and a continuous decrease is observed.

The distinct changes in the pressure behavior of B_0^4 are important with respect to previous superposition model[17] analysis of the high-pressure data.[16] The larger variation observed, when the configuration interactions are taken into account, would lead to a larger variation of the intrinsic parameter. In this sense it would be interesting to reanalyze also the data of $LaCl_3$:Nd^{3+}. For $LaCl_3$:Nd^{3+} a very weak pressure variation of B_0^4 has been observed, which caused severe problems for the determination of the intrinsic parameter.[16] The inclusion of configuration interactions in that case could result in a much stronger variation of B_0^4 and thus could remove the problem with the determination of the intrinsic parameter. In the case of LaOCl:Pr^{3+} the following observations for the crystal-field parameters can be made.

Similar to $LaCl_3$, B_0^6 and B_4^6 did not significantly alter their variations under pressure. Regardless of the configurations involved, both parameters increase in their absolute values. However, in the case of B_0^6 a slightly weaker increase is observed when both excited configurations are taken into account.

In the case of B_0^4 the fit with all configurations distinctly differs from the other cases. In addition to the change in the sign of the ambient pressure value also a change in the direction of the pressure shift is found. In the case of B_4^4 no drastic changes are observed, only in the case where all configurations were taken into account, a slightly different pressure behavior was noticed.

While the pressure variation of B_0^2 does not alter when the $4f^15d^1$ configuration is added, a drastic change is observed when the $4f^16p^1$ configuration is introduced. Instead of a continuous decrease of its absolute value, this parameter first increases and then decreases if all three configurations are taken into account.

Also in the case of LaOCl:Pr^{3+} the superposition model analysis was especially difficult for the $k=4$ parameters. One problem was that the absolute values of the crystal-field parameters could not be reproduced by the intrinsic parameters under pressure.[10] In this case, the configuration interactions could improve the situation because they distinctly change the absolute values as well as the pressure variations of the crystal-field parameters. However, in the present case the changes were found to be insufficient to bring about large improvements. In any case, the large changes in the parameter values as well as in the pressure behavior in some cases, brought about by the configuration interactions, clearly demonstrate the difficulties in using conventional parameters for a more extensive evaluation such as, for example, within the superposition model. The same problem applies for a comparison of experimental crystal-field parameters with *ab initio* calculations. Therefore, the conventional crystal-field parameters should be taken with great care in any case. Actually, it is not a question whether the configuration interactions affect the conventional crystal-field parameters, but the only open point is to what extent they do.

IV. CONCLUSIONS

The energy level variations of $LaCl_3$:Pr^{3+} and LaOCl:Pr^{3+} under pressure have been reanalyzed by taking into account configuration interactions with the excited $4f^15d^1$ and $4f^16p^1$ configurations. To determine specific parameter values as for example the position and the rate of shift for the $4f^15d^1$ configuration, VUV excitation measurements have been carried out.

In general, the configuration interactions cause distinct improvements for the calculation of the $4f^2$ energy levels at ambient as well as at high pressure. In the case of $LaCl_3$:Pr^{3+} the contributions from the $4f^15d^1$ and from the $4f^16p^1$ configurations cause similar and drastic improvements for the description of the $4f^2$ energy levels. The problem of an increasing r.m.s. deviation for the standard fits using only the $4f^2$ configuration can be partly removed by the configuration interactions. The influence of the excited configurations on the free ion parameters $F^k(f,f,f,f)$ and $\zeta(f)$ was found to be negligible. On the contrary, the crystal-

field parameters $B_q^k(f,f)$ show distinct changes in their absolute values and mostly slight changes in their pressure behavior. An exception is made by $B_0^4(f,f)$, which show a much stronger pressure variation when the configuration interactions are taking into account. This observation could solve a special problem that was encountered in an evaluation of this parameter within the superposition model.

For LaOCl:Pr^{3+} the $4f^15d^1$ configuration has a much smaller influence on the $4f^2$ energy levels than the $4f^16p^1$ configuration. Adding the $4f^16p^1$ configuration causes a large improvement in the calculation of the energy levels. However, under pressure the improvement is decreasing which could be caused by the fixing of the free ion parameters $R^k(f,p,f,p)$, which mediate a part of the configuration interactions, or might indicate that the influence of other configurations cannot be discarded. As in the case of $LaCl_3$:Pr^{3+} the influence of the configuration interactions on the free ion parameters $F^k(f,f,f,f)$ and $\zeta(f)$ was negligible. Again, the main effect on the crystal field parameters $B_q^k(f,f)$ is a change in the absolute values, while the pressure behavior is only slightly changed, when all three configurations are taken into account.

The large changes in the absolute values of the crystal-field parameters $B_q^k(f,f)$ as well as individual changes in the pressure behavior reveal difficulties in the use of conventional parameters for more extensive evaluations. These effects point to special caution with respect to further analysis within theoretical models or in comparisons with *ab initio* calculations.

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