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2000 J. Phys.: Condens. Matter 12 6959

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Energy levels of $\text{Pr}^{3+}:\text{GdOCl}$ under pressure

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Received 25 January 2000, in final form 17 April 2000

Abstract. Excitation and luminescence spectra of Pr^{3+} in GdOCl were measured in the spectral range from $11\,000\text{ cm}^{-1}$ to $22\,500\text{ cm}^{-1}$. At ambient pressure a total of 54 spectral lines were observed. Some of these lines cannot be explained by transitions between crystal-field levels of the regular Pr^{3+} site in GdOCl . Possible explanations of these lines are discussed. Under pressure up to 16 GPa, all lines exhibit a red-shift, from which a part of the energy level scheme of the $4f^2$ configuration could be derived. From the 34 levels at ambient pressure, 31 could also be obtained under pressure. The energy level scheme is described in terms of the free-ion parameters (F^k , α , β , γ , ζ , M_k , P^k) and crystal-field parameters (B_0^2 , B_0^4 , B_4^4 , B_0^6 , B_6^6). The variations of these parameters under pressure were determined. Surprisingly, the crystal-field strength, calculated from the crystal-field parameters, first shows a slight decrease with increasing pressure.

1. Introduction

In spite of substantial progress in the description of energy levels of f elements in solids [1], many questions remain. Examples include the problem of correlation crystal fields [1] and the validity of the superposition model [2, 3]. To answer such questions, high pressure is a powerful tool, due to the possibility of continuously changing the crystal-field strength within a particular host crystal [4].

It has been shown that the superposition model was able to describe the crystal fields of $\text{Ln}^{3+}:\text{LaCl}_3$ under pressure [4]. In this case the f element is surrounded by just one type of ligand ions. To test this model also in the more complicated case with two different ligands, $\text{Pr}^{3+}:\text{LaOCl}$ was studied under pressure [5].

In the case of $\text{Pr}^{3+}:\text{LaOCl}$ the description of crystal fields within the superposition model encounters new difficulties. In addition, new lines, which could not be assigned unambiguously, appeared under pressure. In the present work the investigation is extended to $\text{Pr}^{3+}:\text{GdOCl}$, which is studied for the first time. With GdOCl as the host material, it is possible to cover a range of interatomic distances remarkably shorter than in the case of $\text{Pr}^{3+}:\text{LaOCl}$, due to the shorter distances already present at ambient pressure. In addition, it is interesting to see whether new lines also appear in this case, which could help to explain them.

Due to the similarity of the luminescence and excitation spectra of both $\text{Pr}^{3+}:\text{LaOCl}$ and $\text{Pr}^{3+}:\text{GdOCl}$, the former measurements serve as a good starting point for the assignment of the observable spectral lines in the case of $\text{Pr}^{3+}:\text{GdOCl}$. The present experiments were performed with the same experimental set-ups as were used in the former study on $\text{Pr}^{3+}:\text{LaOCl}$ [5].

2. Ambient-pressure results

At ambient pressure it was possible to observe luminescence transitions from the lowest levels of 3P_1 , 3P_0 , and 1D_2 to 3H_J ($J = 4, 5, 6$) and from 3P_0 to 3F_J ($J = 2, 3, 4$). The transitions from 3P_0 dominate all the other lines, while the luminescence from 3P_1 is only weak. From 1I_6 and 3P_2 , no transitions could be observed due to fast non-radiative decay to the lower-lying 3P_0 and 3P_1 multiplets. To gain information about these multiplets and also about the higher levels of 1D_2 , excitation spectroscopy was applied.

Figure 1 gives an overview of the luminescence and excitation spectra of $\text{Pr}^{3+}:\text{GdOCl}$ observed in the range from $11\,500\text{ cm}^{-1}$ to $22\,500\text{ cm}^{-1}$. Most of the luminescence spectra were excited with an argon-ion laser. For those spectra marked with D a dye laser was used to resonantly excite the Pr^{3+} ion. All lines which could not be unambiguously assigned to an electronic transition between crystal-field levels of the Pr^{3+} ion are underlined.

The luminescence and excitation spectra are very similar to those of $\text{Pr}^{3+}:\text{LaOCl}$. However, in view of the number of lines and intensity relations, the pattern of the spectra corresponds not to the ambient-pressure spectra, but to the higher-pressure spectra of $\text{Pr}^{3+}:\text{LaOCl}$. This means also that the unknown lines, which were seen in the case of $\text{Pr}^{3+}:\text{LaOCl}$ only at higher pressures, are already observable at ambient pressure for GdOCl .

In a first approximation, the energy levels and thus the crystal field experienced by the Pr^{3+} ion should be different in the two isostructural hosts only due to the differences in the interatomic distances. At ambient pressure these distances are larger in LaOCl than in GdOCl . Therefore, in principle, the application of pressure to LaOCl should yield conditions similar to those in GdOCl at ambient pressure. In this sense one can expect the observed characteristics of the luminescence and excitation spectra of $\text{Pr}^{3+}:\text{GdOCl}$ to be the same as for $\text{Pr}^{3+}:\text{LaOCl}$ at some higher pressure.

At ambient pressure, 34 energy levels of $\text{Pr}^{3+}:\text{GdOCl}$, as listed in table 1, could be resolved. Besides the similarities in the spectra of $\text{Pr}^{3+}:\text{GdOCl}$ and $\text{Pr}^{3+}:\text{LaOCl}$, there is also an interesting difference. For $\text{Pr}^{3+}:\text{GdOCl}$ the ground state is $^3H_4(\text{E})$; however, for $\text{Pr}^{3+}:\text{LaOCl}$ it is $^3H_4(\text{A}_1)$.

The Hamiltonian for describing the energy level scheme can be divided into free-ion and crystal-field parts. The free-ion part consists of the Coulomb interaction between the f electrons (described by adjustable Slater parameters F^0, F^2, F^4, F^6), the spin-orbit coupling (ζ), the configuration interaction (α, β, γ), minor corrections for spin-spin and spin-other-orbit interactions (M^0, M^2, M^4), and the electrostatically correlated spin-orbit interaction (P^2, P^4, P^6). The second part, the crystal field, is usually represented by the crystal-field parameters B_q^k . In the present case of LnOCl , the point symmetry is C_{4v} ; thus only the parameters $B_0^2, B_0^4, B_4^4, B_0^6, B_4^6$ occur.

With a given energy level scheme, the various parameters belonging to the free-ion and crystal-field part can be fitted to the experimental data. Because of the limited experimental data set, not all parameters could be determined unambiguously. Therefore, the values for some of the free-ion parameters were adopted from LaOCl and kept constant during the fit. The result of the parameter determination for $\text{Pr}^{3+}:\text{GdOCl}$ is shown in table 2. For comparison, the parameter values from the former study on $\text{Pr}^{3+}:\text{LaOCl}$ are also shown.

The free-ion parameters of Pr^{3+} in GdOCl are smaller than those of LaOCl . This is due to the smaller distances within the GdOCl lattice, which cause an increased nephelauxetic effect. The crystal-field parameters B_0^4 and B_4^6 are the same in the two hosts within their mutual errors; however, $B_0^2, B_4^4,$ and B_0^6 show some significant differences. Although the crystal fields can be expected to be different in the two lattices, some of these differences may also be caused by the different data sets available for the respective fits.

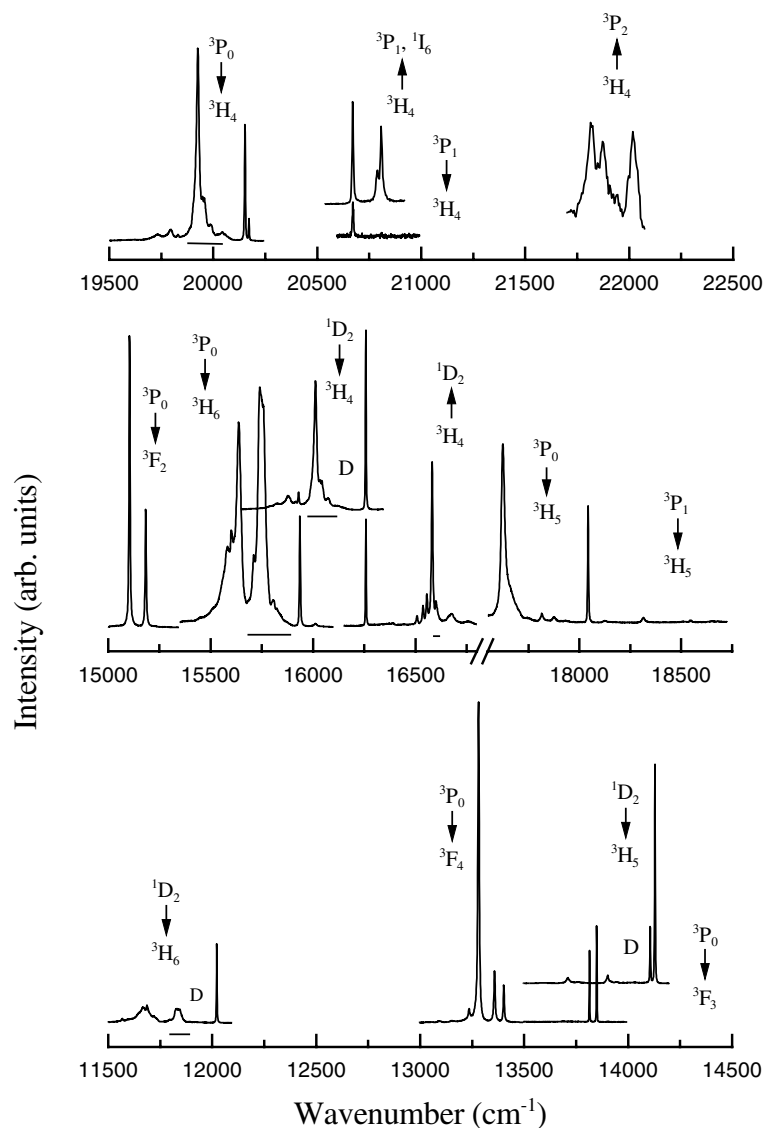


Figure 1. Luminescence (arrows down) and excitation (arrows up) spectra of $\text{Pr}^{3+}:\text{GdOCl}$ at ambient pressure and low temperature (20 K). The luminescence spectra were excited with an argon-ion laser; the spectra marked with D were resonantly excited with a dye laser.

3. High-pressure results

Figure 1 illustrates that the measured luminescence and excitation spectra consist of several groups of lines which correspond to transitions between different crystal-field multiplets. With increasing pressure, the groups shift to lower energies as a whole, due to the weakening of the Coulomb and spin-orbit interaction (the nephelauxetic effect). Besides these shifts, the lines of every group change their mutual distances, due to the change of the crystal field with increasing pressure.

Under pressures up to 16 GPa it was possible to follow 31 of the 34 energy levels det-

Table 1. Experimental and calculated energy levels of Pr³⁺:GdOCl at ambient pressure.

Level	Energy (cm ⁻¹)		Level	Energy (cm ⁻¹)		
	Experimental	Calculated		Experimental	Calculated	
³ H ₄	E	0.0	18.1	³ F ₄ A ₁	6814.1	6799.1
	A ₁	19.1	8.2	A ₂	—	6820.5
	B ₁	—	123.5	B ₂	—	6848.7
	E'	246.1	207.6	E'	6890.8	6906.6
	B ₂	328.7	345.4	A' ₁	6936.3	6950.5
	A ₂	—	408.7			
	A' ₁	—	422.2	¹ G ₄ B ₁	—	9519.1
			E	—	9760.0	
³ H ₅	A ₂	2121.2	2126.5	A ₁	—	9800.2
	E	2129.2	2142.2	A ₂	—	9851.6
	B ₂	2152.2	2177.4	B ₂	—	9742.1
	B ₁	—	2371.4	E'	—	9986.6
	E'	2356.7	2337.5	A' ₁	—	10094.7
	A ₁	2296.2	2279.9			
	A' ₂	—	2322.0	¹ D ₂ B ₂	16258.5	16237.1
	E''	2547.3	2511.9	B ₁	16507.6	16537.6
			A ₁	16556.7	16561.9	
³ H ₆	A ₁	4159.4	4179.6	E	—	16644.3
	E	4236.1	4249.7			
	B ₁	—	4324.2	³ P ₀ A ₁	20171.6	20173.2
	A ₂	—	4471.5			
	E'	—	4405.6	³ P ₁ A ₂	20671.6	20676.6
	B ₂	—	4532.3	E	20808.5	20823.0
	A' ₁	4533.7	4515.8			
	E''	4570.2	4570.6	¹ I ₆ A ₁	—	20830.8
	B' ₁	—	4780.1	E	20814.1	20804.7
	B' ₂	—	4783.5	B ₂	20814.1	20803.1
			B ₁	—	21110.6	
³ F ₂	B ₁	—	4938.8	E'	—	21143.7
	B ₂	—	4982.7	A ₂	—	21261.7
	E	4988.5	5003.6	A' ₁	—	21334.5
	A ₁	5067.4	5064.0	E''	—	21475.6
				B' ₂	21406.7	21409.5
³ F ₃	E	6322.8	6314.3	B' ₁	—	21414.3
	B ₁	—	6351.4			
	E'	6357.1	6362.5	³ P ₂ B ₂	21816.7	21795.1
	B ₂	—	6390.4	B ₁	21875.5	21855.8
	A ₂	—	6468.6	E	—	22009.4
			A ₁	22020.0	22038.3	
³ F ₄	B ₁	—	6720.3			
	E	6769.5	6777.5	¹ S ₀ A ₁	—	45960.1

ermined at ambient pressure, due to the fact that with increasing pressure some lines lose intensity and in addition an inhomogeneous line broadening is caused by non-hydrostatic conditions within the sample. Both effects lead to the vanishing of some lines which were

Table 2. Free-ion and crystal-field parameters (in cm^{-1}) for Pr^{3+} in GdOCl and LaOCl at ambient pressure. Uncertainties are given in brackets. Asterisks mark parameters which were kept fixed during the fits.

	$\text{Pr}^{3+}:\text{GdOCl}$		$\text{Pr}^{3+}:\text{LaOCl}$	
E_{ave}	9895	(8)	9968	(8)
F^2	67006	(46)	67305	(36)
F^4	49954	(206)	50107	(184)
F^6	32709	(109)	32999	(96)
ζ	739.5	(2.2)	742.0	(1.7)
α	22	(*)	22	(*)
β	-700	(*)	-700	(*)
γ	1422	(*)	1422	(*)
M_0	1.76	(*)	1.76	(*)
P^2	275	(*)	275	(*)
B_0^2	-554	(23)	-859	(22)
B_0^4	-470	(89)	-437	(72)
B_4^4	± 709	(42)	± 945	(32)
B_0^6	1175	(101)	652	(95)
B_4^6	± 69	(127)	± 155	(85)
N	34		37	
σ	20.4		16.6	

already weak at ambient pressure.

As an example, figure 2 shows the luminescence spectra for the transitions ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ at various pressures. Within the C_{4v} point symmetry, three transitions from the occupied ${}^1\text{D}_2(\text{B}_2)$ level are electric dipole allowed and were assigned as shown in figure 2. This assignment is consistent with former results on $\text{Pr}^{3+}:\text{LnOCl}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Gd}$) [5–7].

The origin of the additional lines a and b is not well understood. According to the ambient-pressure spectrum, one may assign lines a and b simply to vibronic lines of the ${}^1\text{D}_2(\text{B}_2) \rightarrow {}^3\text{H}_4(\text{E})$ transition. These lines were studied in detail for $\text{Pr}^{3+}:\text{LaOCl}$ [7]. However, according to the spectra presented in reference [7], vibronic lines can be expected not only in a small region around 220 cm^{-1} below the zero-phonon line, but also in a rather broad spectral range. In addition, there is no reasonable explanation for why these two lines in particular should show a distinct increase in intensity, while no other bands can even be observed under pressure. Therefore, it seems unlikely that the lines a and b can be assigned to vibronic transitions.

With increasing pressure a drastic change in the relative intensities of the lines ${}^1\text{D}_2(\text{B}_2) \rightarrow {}^3\text{H}_4(\text{E}')$, a and b, can be seen. The assignment at higher pressures, shown in figure 2, is confirmed by plotting the shifts of the luminescence lines as a function of pressure in figure 3. Similar observations were made already for $\text{Pr}^{3+}:\text{LaOCl}$ under pressure [5]. Whereas at ambient pressure, for example the ${}^3\text{P}_0(\text{A}_1) \rightarrow {}^3\text{H}_4(\text{E}')$ transition was observable in LaOCl , with increasing pressure three new lines emerged in the vicinity of this transition. At the same time the ${}^3\text{P}_0(\text{A}_1) \rightarrow {}^3\text{H}_4(\text{E}')$ line completely changed its former variation with pressure and lost intensity, until it disappeared almost completely around 36 GPa. Thus, at high pressures only the three new and unidentified lines remained.

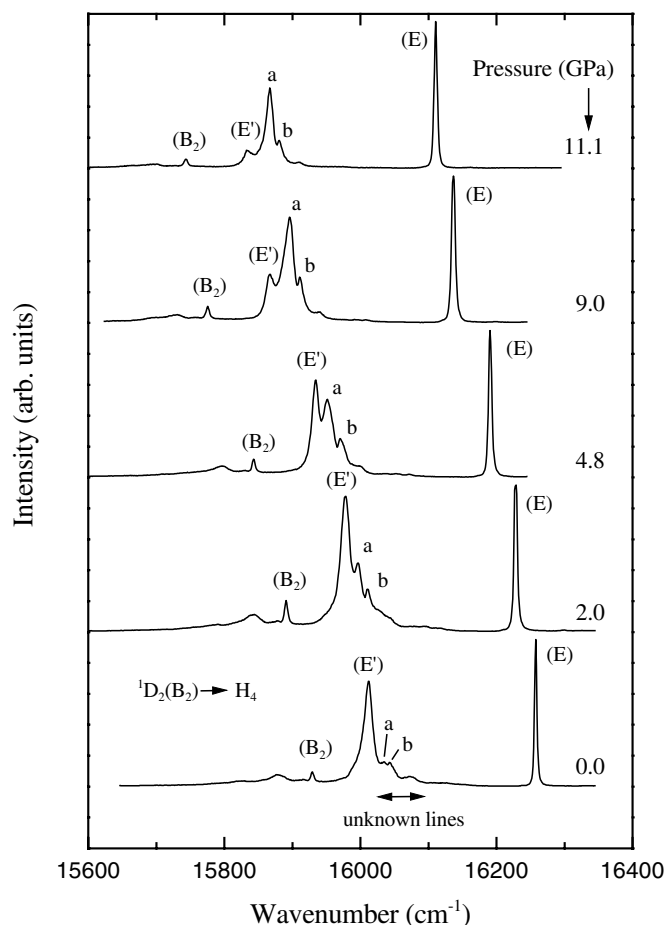


Figure 2. Luminescence spectra of the transitions ${}^1D_2(B_2) \rightarrow {}^3H_4(E')$ of $Pr^{3+}:GdOCl$ at various pressures and 20 K. Lines marked a and b denote unknown lines.

In the case of $GdOCl$ the unknown lines (a, b) are already visible at ambient pressure, which fits with the observation that the high-pressure spectra of $LaOCl$ can be related to the ambient-pressure spectra of $GdOCl$. However, following this observation, the assignment of the ${}^1D_2(B_2) \rightarrow {}^3H_4(E')$ transition under pressure may be doubtful, because analogously to the case of $LaOCl$ the variation with pressure may already be disturbed for similar reasons to in the case of $LaOCl$ [5]. Indeed, the high-pressure fits resulted in a steadily increasing deviation between the experimental and calculated ${}^3H_4(E')$ level. Due to these uncertainties, fits without this level were also performed. In this case the standard deviation is distinctly decreasing; however, the variations of the free-ion and crystal-field parameters were only slightly affected. Therefore, despite the uncertainties in the ${}^3H_4(E')$ level, it was taken into account in the fits presented here.

It is possible to explain the additional lines by a relaxation of the C_{4v} point symmetry around the Pr^{3+} ion due to splittings of degenerate lines in a lower symmetry. However, since ${}^3H_4(E')$ is only a doubly degenerate state, only one further line can be explained by a reduced symmetry. Furthermore, a relaxation of the point symmetry should also result in splittings of other E levels, for example ${}^3H_4(E)$ or ${}^3H_5(E, E', E'')$. This is not observed in the spectra,

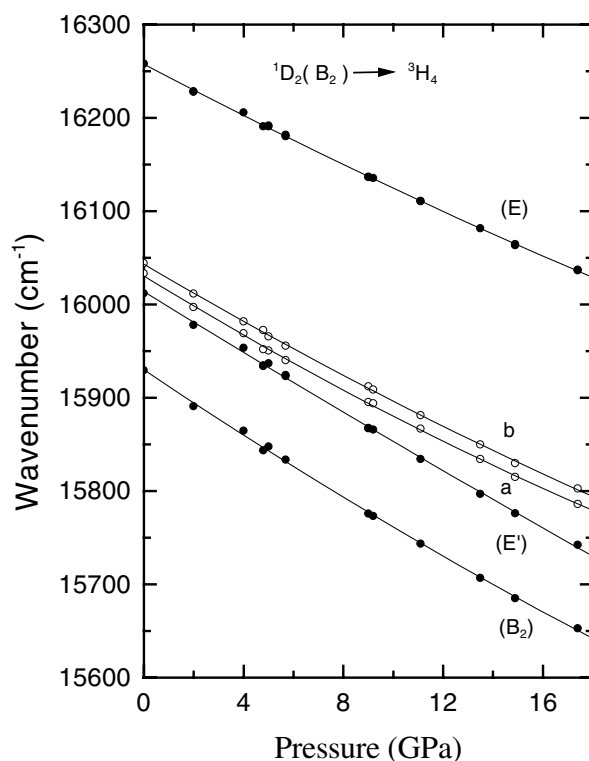


Figure 3. Shifts of the luminescence transitions ${}^1D_2 \rightarrow {}^3H_4$ of $\text{Pr}^{3+}:\text{GdOCl}$ under pressure at 20 K. Lines marked a and b denote unknown lines.

which means either that only the splitting of ${}^3H_4(E')$ is large enough to become observable or that the new lines cannot be explained by a symmetry-induced splitting. In addition, x-ray diffraction studies on LnOCl materials ($\text{Ln} = \text{La}, \text{Pr}, \text{Gd}$) did not indicate any phase transition under pressure. Therefore, a reduced point symmetry seems to be unlikely.

To check the possibility of the unidentified lines originating from a different Pr^{3+} site in LnOCl , excitation spectra were taken for these lines. However, the spectra did not show any difference from those excitation spectra which were taken for the clearly assigned transitions of the ordinary rare-earth site in LnOCl . Thus, a different site can be ruled out also.

A further reason for the observation of these new lines may be given in terms of electron-phonon interaction, which can lead to a splitting of electronic lines [8]. This possibility has already been discussed in the case of $\text{Pr}^{3+}:\text{LaOCl}$ [5]. To check such an interpretation it would be necessary to study phonon energies under pressure, for instance by means of Raman scattering.

A typical example for the excitation spectra under pressure is shown in figure 4. In this range the transitions ${}^3H_4 \rightarrow {}^3P_1$ and ${}^3H_4 \rightarrow {}^1I_6$ can be observed. As in the case of $\text{Pr}^{3+}:\text{LaOCl}$ [5], the much stronger shift of the 3P_1 levels with respect to the 1I_6 levels is clearly visible. The two transitions to the 1I_6 multiplet, ${}^3H_4(E) \rightarrow {}^1I_6(E)$ and ${}^3H_4(E) \rightarrow {}^1I_6(B_2)$, are not separated in the lower-pressure range. Only above around 13 GPa are these lines well resolved. The strong line visible in the spectrum at 13.8 GPa on the high-energy side can be assigned most probably to the ${}^3H_4(E) \rightarrow {}^1I_6(A_1)$ transition.

From the spectral lines observed and assigned in luminescence and excitation spectra of

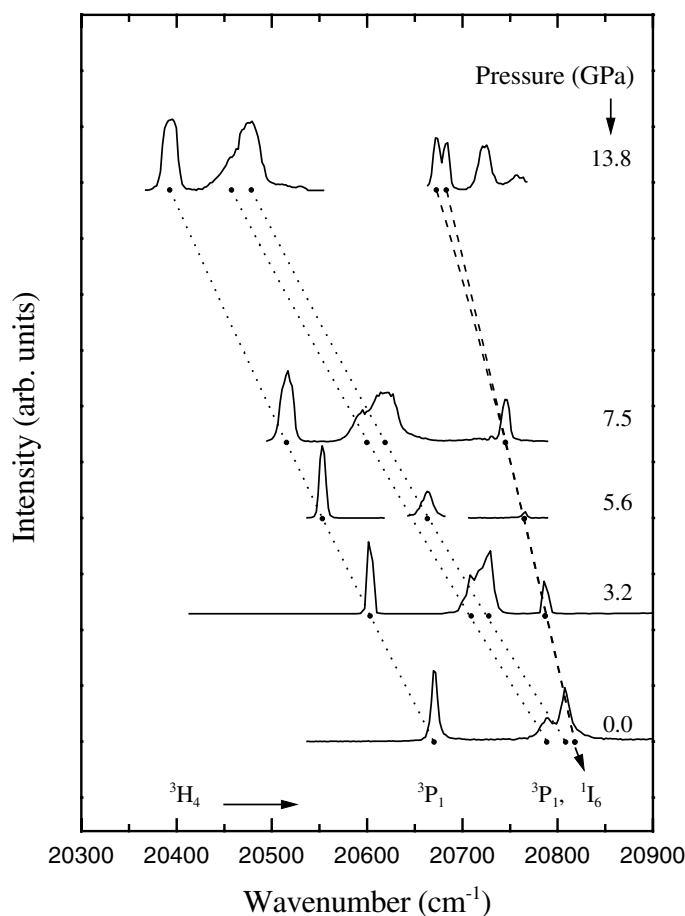


Figure 4. ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ and ${}^3\text{H}_4 \rightarrow {}^1\text{I}_6$ transitions in the excitation spectra of $\text{Pr}^{3+}:\text{GdOCl}$ at various pressures and approximately 20 K. Clearly visible are the different shifts of the ${}^1\text{I}_6$ and ${}^3\text{P}_2$ levels.

$\text{Pr}^{3+}:\text{GdOCl}$, 31 energy levels are determined up to 16 GPa and used in the parameter fitting.

According to the nephelauxetic effect, the free-ion parameters F^k and ζ decrease with increasing pressure. The relative decreases of these parameters up to 16 GPa are shown in table 3. For comparison, the results for $\text{Pr}^{3+}:\text{LaOCl}$ are also included in the table. In both cases the analysis yields $\Delta F^2/F^2 > \Delta F^4/F^4 > \Delta F^6/F^6$. This is an observation which was made also for other f elements in different host materials [4,9].

Table 3. Relative decreases of free-ion parameters (in %) for Pr^{3+} in GdOCl and LaOCl up to 16 GPa.

	$\text{Pr}^{3+}:\text{GdOCl}$		$\text{Pr}^{3+}:\text{LaOCl}$	
E_{ave}	-1.1	(1)	-1.3	(1)
F^2	-1.7	(1)	-1.5	(1)
F^4	-0.9	(1)	-1.0	(1)
F^6	-0.3	(2)	-0.5	(2)
ζ	-0.6	(2)	-1.0	(1)

The relative decrease of the spin-orbit coupling parameter ζ is obviously smaller than the relative change of F^2 . This is also consistent with former results [4,9]. A comparison of these shifts allows us to draw the same conclusions with respect to the nephelauxetic effect as in the case of $\text{Pr}^{3+}:\text{LaOCl}$ [5]. A quantitative analysis of the nephelauxetic effect under pressure for a series of $\text{Pr}^{3+}:\text{LnOCl}$ samples is currently in progress [10].

The changes of the crystal-field parameters with increasing pressure are represented in figure 5. The dependence of the crystal-field parameters on the set of energy levels available for the fits affects primarily the absolute parameter values, whereas the pressure behaviour remains qualitatively the same.

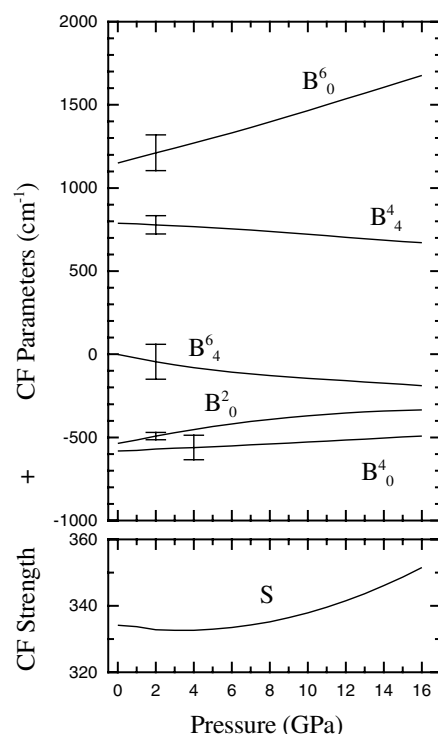


Figure 5. Crystal-field parameters B_q^k ($kq = 20, 40, 44, 60, 64$) for $\text{Pr}^{3+}:\text{GdOCl}$ under pressure. Also shown is the crystal-field strength S .

From the equation

$$S = \left\{ \frac{1}{3} \sum_k \frac{1}{2k+1} \left[B_{k0}^2 + 2 \sum_{m>0} (\Re B_{km}^2 + \Im B_{km}^2) \right] \right\}^{1/2} \quad (1)$$

it is possible to deduce an overall crystal-field strength [11] which is also shown in figure 5.

The crystal-field strength for $\text{Pr}^{3+}:\text{GdOCl}$ shows a slight decrease in the low-pressure range and increases only after passing through a minimum at about 4 GPa. A decrease of the crystal-field strength S was also found in the case of $\text{Pr}^{3+}:\text{LaOCl}$ [5]. However, in that case no minimum could be reached up to 16 GPa.

A decreasing crystal-field strength at first seems surprising. Because of decreasing interatomic distances under pressure, the interactions between the f electrons and the ligands should become stronger. This in turn should lead to an increase in the crystal-field strength.

To explain the decrease at least qualitatively, the superposition model [2, 3] can be used. Within this model, the crystal-field parameters B_q^k can be split up into distance-dependent parts multiplied by angular factors, which describe the geometrical arrangement of the next-nearest-neighbour ions around the Pr^{3+} ion. The distance-dependent parts are the intrinsic parameters \overline{B}_k , which reflect the interaction between the f electrons and a single ligand.

Ab initio calculations of the intrinsic parameters for chloride ions revealed that these parameters show the expected increase with decreasing distances [12]. However, because of the geometrical factors, this does not necessarily mean that the overall crystal-field strength must also increase. On the contrary, special changes in the bonding angles can occur under pressure (without changing the point symmetry), which may indeed result in a decrease of the total crystal-field strength.

In this sense one can compare also the behaviour of LaOCl with that of GdOCl. Because LaOCl has much larger bonding distances, it should act as GdOCl but with a high *negative* pressure. Therefore, a minimum and a subsequent increase in the crystal-field strength can be expected in LaOCl only at very high pressures.

Recent x-ray diffraction and EXAFS measurements on LaOCl and GdOCl [13] are expected to determine the interatomic distances and angles for both host materials. With this structural information it would be possible to evaluate the pressure dependence of the geometrical factors used in the superposition model more quantitatively.

4. Conclusions

Luminescence and excitation spectra of $\text{Pr}^{3+}:\text{GdOCl}$ were studied under pressures up to 16 GPa. The ambient-pressure spectra are found to be very similar to those of $\text{Pr}^{3+}:\text{LaOCl}$ at high pressure. In particular, some unknown spectral lines, occurring in LaOCl only at high pressure, are already observed in $\text{Pr}^{3+}:\text{GdOCl}$ at ambient pressure. A convincing explanation for the occurrence of these lines is still lacking.

From the luminescence and excitation spectra of $\text{Pr}^{3+}:\text{GdOCl}$ it was possible to determine the energy level scheme under pressure up to 16 GPa at least partly. The pressure shifts of the energies can be explained by changes of the free-ion and crystal-field parameters. The free-ion parameters decrease under pressure in a similar way to that already observed for $\text{Pr}^{3+}:\text{LaOCl}$.

The crystal-field strength first decreases and then passes through a minimum at around 4 GPa. This peculiar behaviour can be explained qualitatively within the superposition model, by changes in the geometrical factors.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) under grant number HO 486/21 and, for the use of LENS, by the European Community under contract No ERB FMGE*CT95-0017. WBH thanks LENS and its staff for their hospitality.

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