PHYSICAL REVIEW B VOLUME 48, NUMBER 5 1 AUGUST 1993-I

Energy levels of Nd^{3+} and Pr^{3+} in $R$$Cl_3$ under pressure

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(Received 4 December 1992; revised manuscript received 5 April 1993)

The fluorescence of Pr^{3+}:$LaCl_3$, $PrCl_3$ and Nd^{3+}:$LaCl_3$, $NdCl_3$ has been measured up to pressures of 10 GPa. In addition the structural parameters of $PrCl_3$ and $GdCl_3$ have been obtained up to 8 GPa. From the pressure shifts of the energy levels the Slater parameters F^k, the spin-orbit-coupling parameter ζ and the crystal-field splittings are derived. The crystal-field parameters B_q^k are determined taking into account the effects of J mixing. In spite of their different electronic configurations, the crystal-field parameters for Pr^{3+} and Nd^{3+} show a very similar behavior under pressure. It is shown that the superposition model can qualitatively describe the observed variations of the crystal-field parameters of rank four and six.

I. INTRODUCTION

Trivalent lanthanide ions in the isostructural trichlorides of lanthanum to gadolinium provide simple model systems for high-pressure spectroscopic and crystal-field studies. This is due to (i) excellent optical properties like transparency, weak contributions from crystal vibrations, strong fluorescence also in the pure trichlorides and very sharp lines, (ii) no local distortions in the pure crystals, and (iii) detailed experimental and theoretical information about the nature of the energy levels of lanthanide ions in $LaCl_3$ at ambient pressure.

By measuring the effect of pressure on the crystal structure of the host lattice and on the optical spectra of the lanthanide ion in the same host crystal, the structural dependence of the lanthanide $4f^N$ energy levels can be obtained. This in turn provides a basis for testing various models describing the $4f^N$ energy-level schemes.

In addition to our previous high-pressure studies on Pr^{3+}:$LaCl_3$ (Ref. 1) and Nd^{3+}:$LaCl_3$ (Ref. 2), results for the pure systems are reported here. Besides the extension to the pure crystals, the present study includes a detailed comparison of the results for $4f^2$ and $4f^3$ configurations. The evaluation of the data also takes into account effects of J mixing and an expanded free-ion Hamiltonian.

The present paper summarizes these results and shows that the experimental data provide a consistent picture for the pressure dependence of the $4f^N$ energy levels. An analysis of these results within the superposition model suggests that the superposition model can account for the internuclear distance dependence of the forth and sixth rank crystal-field parameters.

II. EXPERIMENTAL DETAILS

The crystals used for this study were grown from high-purity anhydrous trichlorides in the materials laboratory of the University of Paderborn using standard procedures.[3] The doped samples of $LaCl_3$ contained 1 mol % Pr^{3+} or Nd^{3+}, respectively.

The fluorescence was excited with an argon-ion laser and measured at temperatures of about 20 and 100 K. The temperatures of 20 K were attained with a closed-cycled refrigerator and a specially adapted small diamond-anvil cell with a diameter of 26 mm and a height of 20 mm. Temperatures of 100 K were attained with a liquid-nitrogen-bath cryostat and a diamond-anvil cell of the Syassen-Holzapfel type.[4,5]

As a pressure transmitting medium, either Heptane or spectroscopy (polychlorotrifluoroethylene) oil were used. Pressures were determined by the ruby fluorescence method using the linear ruby scale with $d\nu/dp=7.53$ cm^{-1}/GPa (Ref. 6) and constant thermal corrections.[7] Structural studies of the host lattices $LaCl_3$, $PrCl_3$, and $GdCl_3$ were performed by single-crystal and powder x-ray-diffraction techniques.[8,9]

III. STRUCTURAL DEPENDENCE OF $LnCl_3$

The anhydrous trichlorides of the lanthanides from lanthanum to gadolinium crystalize under normal conditions in the hexagonal UCl_3 type structure[10,11] (space group $P6_3/m$ or C_{6h}^2) with the lanthanide ion in the $2d$ positions $\pm(2/3,1/3,1/4)$ and Cl in the $6h$ positions $\pm(x,y,1/4;\bar{y},x-y,1/4;y-x,\bar{x},1/4)$. The site symmetry of lanthanide and chlorine ions is thereby $\bar{6}(C_{3h})$ and $m(\sigma_h)$, respectively.

As shown in Fig. 1, the lanthanide coordination polyhedron consists of nine chlorine ligands arranged on a tricapped trigonal prism. The capping ligands, referred to as equatorial, are at the distance R_E and the apical ones at the distance R_A, with respect to the central ion. The polar angle of the apical anions with respect to the crystallographic c axis is denoted by θ, and the angular deviation of the equatorial anions from the normal of the prism faces is denoted by δ. The variation of R_E, R_A, θ, and δ for $LaCl_3$, $PrCl_3$, and $GdCl_3$ at room temperature under pressures up to 8 GPa are represented in Figs. 2(a)–2(c). In all cases the data show similar variations of the structural parameters for these coordination polyhedra.

Energy dispersive x-ray-diffraction studies on polycrystalline $LaCl_3$ samples in the more extended pressure

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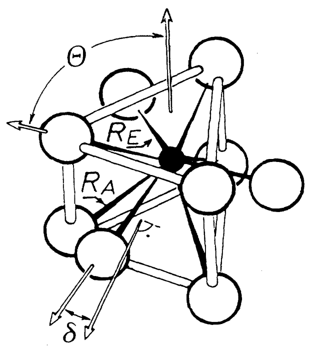

FIG. 1. Polyhedron of the Cl ligands in $LnCl_3$. R_E and R_A denote the equatorial and apical Ln—Cl bond distances, respectively. Θ denotes the polar angle of the apical anions and δ the deviation from the normal of the prism faces to the equatorial anions.

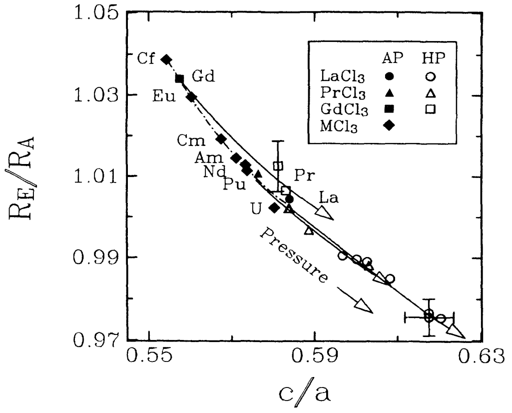

FIG. 3. R_E/R_A vs c/a for lanthanide and actinide trichloride compounds at ambient (AP) and high pressure (HP).

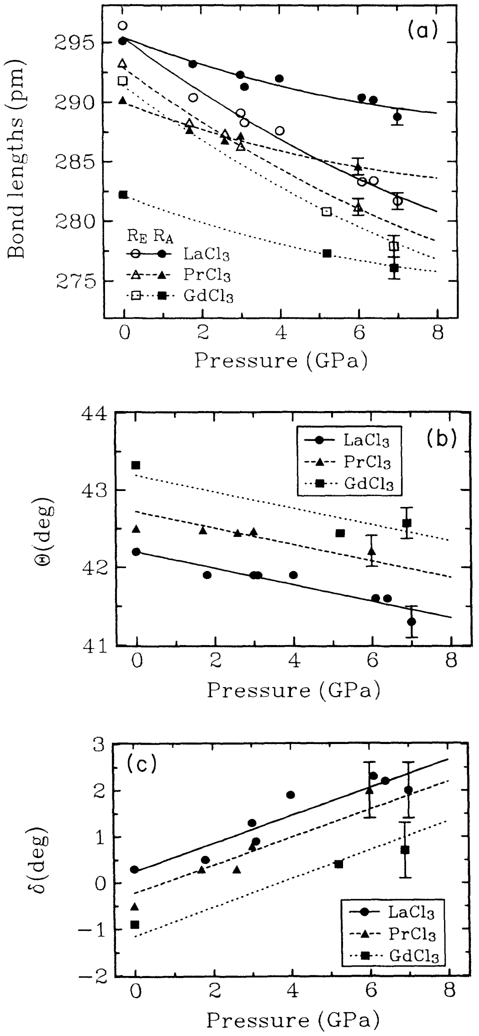

FIG. 2. Variation of the bond distances R_E and R_A of $LnCl_3$ under pressure, (b) Variation of angle Θ of $LnCl_3$ under pressure, (c) Variation of angle δ of $LnCl_3$ under pressure.

range up to 33 GPa show the appearance of new weak diffraction lines at about 5 GPa and give strong indications of a structural phase transition of the whole sample at about 14 GPa. We have also studied the Raman spectra of single crystals of $LaCl_3$ and $GdCl_3$ which support this observation of a structural phase transition between 10 and 14 GPa. We believe that the main reason for the reported anomalies of Pr^{3+}:$LaCl_3$ (Ref. 1) are due to this phase transition.

Figure 3 shows the experimental results for ratio R_E/R_A vs c/a for some lanthanide[12] and actinide[13] compounds at ambient pressure together with the high-pressure data for $LaCl_3$, $PrCl_3$, and $GdCl_3$. It is obvious that increasing pressure is homologous to decreasing atomic number. Because all lanthanides studied under pressure exhibit a similar variation, we adopt this variation for $NdCl_3$, taking as the starting point the ambient pressure values from the literature.[12]

IV. ENERGY LEVELS OF Ln^{3+} UNDER PRESSURE

A detailed discussion of pressure effects on fluorescence and energy levels of Pr^{3+}:$LaCl_3$ has been given before[1] and thus will be omitted here. Very similar behavior under pressure is also observed for Pr^{3+}:$PrCl_3$. Line shifts on the order of 25 cm^{-1}/GPa are typical for both host lattices. At ambient conditions a small redshift of the energy levels of Pr^{3+}:$PrCl_3$ is observed when compared to Pr^{3+}:$LaCl_3$. Thus at a pressure of about 0.9 GPa the energy levels of Pr^{3+}:$LaCl_3$ are close to those of Pr^{3+}:$PrCl_3$ at ambient pressure.

Since the fluorescence from $^3P_1$ to lower states was not recorded in the case of Pr^{3+}:$PrCl_3$, only three levels of $^3H_4$ and $^3F_4$, two levels of $^3H_5$ and $^3H_6$, and one level of $^3F_2$ and $^3P_0$ could be determined in the present study.

When one compares the variation of the 12 measured energy levels of Pr^{3+}:$PrCl_3$ with the variation of the same levels of Pr^{3+}:$LaCl_3$, one finds only two levels, $^3H_4(2')$ and $^3F_4(2')$, with different behavior under pressure. In these two cases the levels were derived from only one fluorescence line whereby the weak fluorescence line to $^3H_4(2')$ overlaps with a stronger line. Therefore the determination of this energy level is quite uncertain.

The pressure dependence of 30 crystal-field energy levels of the $^4I_{9/2,11/2}$, $^4F_{3/2,5/2}$, $^2H(2)_{11/2}$, $^4G_{7/2}$, $^2G_{9,2}$, and $^2D_{3/2}$ multiplets have been obtained by measuring the fluorescence of Nd^{3+}:$LaCl_3$ up to pressures of 10 GPa. More than 200 fluorescence lines were observed at ambient pressure; however, due to the broadening of the weak lines, only 80 lines could be followed under pressure. The shift of these fluorescence lines under pressure typically amounts to 13 cm^{-1}/GPa. As an example, Fig. 4(a) shows the effect of pressure on the energy levels of the anomalous $^2H(2)_{11/2}$ multiplet of Nd^{3+}:$LaCl_3$.

In the case of Nd^{3+}:$NdCl_3$ the spectra exhibit a smaller number of fluorescence lines so only 16 crystal-field levels of the $^4I_{9/2,11/2}$, $^4G_{5/2}$, $^4G_{7/2}$, and $^2D_{3/2}$ multiplets have been obtained. The average shift of the fluorescence lines is somewhat larger than for Nd^{3+}:$LaCl_3$. At a pressure of about 1.3 GPa the energy levels of Nd^{3+}:$LaCl_3$ are close to the levels of Nd^{3+}:$NdCl_3$ at ambient pressure [see Fig. 4(b)].

The comparison of the results for the two different ions Pr^{3+} and Nd^{3+} shows that the line shifts for Pr^{3+} are approximately twice as large as for Nd^{3+}. On the other hand, the line shifts for the same ion in different hosts show, at the most, about 15% differences.

V. PARAMETRIC RESULTS

For energy-level calculations of lanthanide ions, one considers first the atomic free-ion part and then a perturbed crystal field produced by the other ions in the host crystal. In the phenomenological scheme the various interactions contributing to the Hamiltonian are theoretically split into the unknown radial parts which are treated as adjustable parameters and the angular parts which can be calculated exactly.

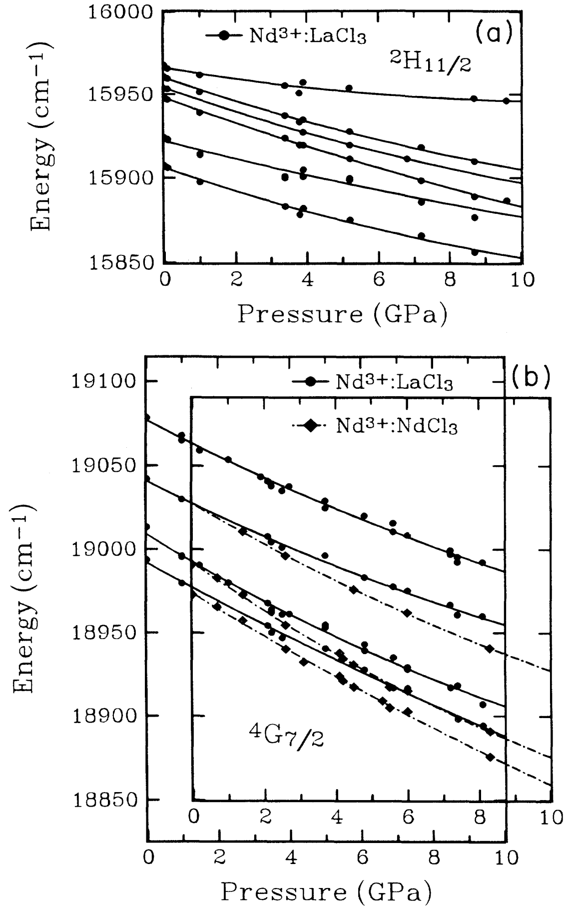

FIG. 4. (a) Energy-level shifts of $^2H(2)_{11/2}$ for Nd^{3+}:$LaCl_3$ under pressure, (b) Energy-level shifts of $^4G_{7/2}$ for Nd^{3+}:$LnCl_3$ under pressure. The energy levels of Nd^{3+}:$NdCl_3$ are shifted by a pressure of 1.3 GPa with respect to Nd^{3+}:$LaCl_3$.

A detailed description of the free-ion Hamiltonian has been given in Ref. [14] and will thus be omitted here. The matrix elements of the free-ion Hamiltonian $H_{\rm FI}$ can be written as follows:

$$\langle |H_{\rm FI}|\rangle = \sum_k F^k f_k + \zeta\left\langle \left|\sum_i s_i l_i\right|\right\rangle + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_\lambda T^\lambda t_\lambda + \sum_k P^k p_k + \sum_k M^k m_k \,, \tag{1}$$

where the f_k, t_λ, p_k, and m_k are expectation values of operators acting only on the angular parts of the wave functions, s_i and l_i are the spin and orbital angular momentum of the ith electron, L is the total orbital angular momentum, and $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operators for the groups G_2 and R_7.

The crystal field is introduced as a perturbative potential added to the free-ion Hamiltonian. The potential in the one-electron approximation can be written as follows:

$$H_{\rm CF} = \sum_{k,q} B_q^k C_q^k \,,$$

where the C_q^k are tensor operators.[15] The matrix elements of the tensor operators can be calculated exactly, whereas the B_q^k are regarded as adjustable crystal-field parameters. The number of parameters for this potential is determined by the parity and triangular selection rules[16] and the point symmetry at the site of the lanthanide ion. The point symmetry in the trichlorides is C_{3h}. Therefore the number of crystal-field parameters is five, including the occurrence of an imaginary part of the parameter B_6^6. Since rotation of the coordinate system reduces the number of parameters to only four, one can work with an effective D_{3h} symmetry.[15]

Thus the crystal-field Hamiltonian with a D_{3h} symmetry can be written as follows:

$$H_{\mathrm{CF}}=B_0^2C_0^2+B_0^4C_0^4+B_0^6C_0^6+B_6^6(C_6^6+C_{-6}^6)\ ,$$

with only four (real) crystal-field parameters B_q^k.

A. Ambient pressure results

Table I shows the results of least-squares fits for Nd^{3+}:LaCl$_3$ and Pr^{3+}:LaCl$_3$ using experimental data from the literature.[14,17,18] N denotes the number of levels used and σ gives the standard deviations obtained in these fits. The parameters P^k and M^k are coupled by their Hartree-Fock ratios from the literature.[19] Therefore only two effective parameters, one for all P^k and one for all M^k, were used.

Small changes in the free-ion and crystal-field parameters for the restricted high-pressure (HP) data sets in comparison with the results for the more extended data sets from the literature[14,17,18] can be seen in Table I. However, due to the fixed number of levels used in the high-pressure experiment, one expects that these systematic errors change only slightly under pressure. In any case these systematic uncertainties are small compared with the variation of the parameters under pressure.

B. Free-ion parameters under pressure

The number of adjustable parameters in the free-ion Hamiltonian exceeds the number of terms obtained under pressure. Therefore it was not possible to vary all these parameters freely. Because the main contributions to the energies of the terms originate from the coulomb and spin-orbit interaction, only the Slater and spin-orbit-coupling parameters were varied.

The influence of the other parameters on the shifts of the energy levels should be small compared to the shift due to changes of F^k and ζ. Nevertheless, it is possible that the evaluated variation of the Slater and the spin-orbit-coupling parameters would change, if one allows all parameters to vary freely. The largest changes are expected to result from changes of the two-electron electrostatic interactions and are found to have negligible effects on the other parameters. The magnitude of these effects can be estimated, for instance, by assuming a linear dependence of the changes of α and β on V_0/V. The values for the free-ion PrIV (Ref. 20) correspond to $V_0/V=0$, the values for Pr^{3+}:LaCl$_3$ at ambient pressure refer to $V_0/V=1$, and for Pr^{3+}:LaCl$_3$ at 8 GPa belong to $V_0/V=1.17$. Then the variation of α and β up to 8 GPa would be expected to amount to 17% of the change between the free ion and the ambient pressure values.

In addition, if a fixed ratio of α/γ is assumed as proposed by Goldschmidt *et al.*,[21] the estimated variations are $\Delta\alpha/\alpha_0=-0.8\%$, $\Delta\beta/\beta_0=-2.1\%$, and $\Delta\gamma/\gamma_0=-0.8\%$. With these variations we repeated the least-squares fits of Pr^{3+}:LaCl$_3$. As the result the variation of the Slater and spin-orbit-coupling parameters changes only insignificantly under pressure. The largest deviation shows F^4 and the relative decrease of this parameter

TABLE I. Energy parameters (in cm^{-1}) for Pr^{3+}:LaCl$_3$ and Nd^{3+}:LaCl$_3$ at ambient pressure with statistical uncertainties given in ( ). Parameters derived with the present program from the more extended data sets given in the literature (Refs. 14, 17, and 18) are shown for comparison. The values with (l_*) were not varied in the fits of the more restricted data sets obtained under high pressure (HP). The number of levels used in these different fits is given by N and σ denotes the standard deviation between measured and calculated energy levels.

Parameter	Pr^{3+}:LaCl$_3$		Nd^{3+}:LaCl$_3$	
E_{ave}	9932 (3)	9931 (3)	24 178 (4)	24 178 (5)
F^2	68 399 (16)	68 438 (10)	71 925 (20)	71 922 (22)
F^4	50 173 (40)	50 227 (21)	52 168 (46)	52 259 (37)
F^6	32 909 (35)	32 974 (13)	35 502 (25)	35 488 (44)
ζ	746.3 (4)	746.0 (1.1)	876.2 (5)	874.9 (1.0)
α	22.81 (*)	22.81 (10)	22.16 (*)	22.16 (8)
β	−676 (*)	−676 (7)	−654 (*)	−654 (5)
γ	1453 (*)	1453 (6)	1565 (*)	1565 (10)
T^2			361 (*)	361 (10)
T^3			40 (*)	40 (2)
T^4			60 (*)	60 (2)
T^6			−293 (*)	−293 (4)
T^7			349 (*)	349 (7)
T^8				355 (*)
M^0	1.72 (*)	1.72 (13)	1.92 (*)	1.92 (9)
P^2 266 (*)		266 (24)	288(*)	288 (20)
B_0^2	118 (7)	106 (5)	145 (18)	153 (7)
B_0^4	−334 (12)	−333 (10)	−260 (32)	−347 (15)
B_0^6	−668 (17)	−652 (15)	−680 (27)	−714 (16)
B_0^6	442 (11)	447 (10)	485 (21)	468 (13)
N	29	61	30	127
σ	5.5	7.3	8.9	8.9
	(HP)	(23)	(HP)	(22)

changes from −0.78% to −0.84%.

Possible effects from other higher-order parameters are expected to be even smaller than the changes due to α, β, and γ, and therefore it seems reasonable to fix all higher-order parameters to their ambient pressure values. For the pure crystals we have taken these values from the doped $LaCl_3$, since the pressure shifts for the pure and the doped crystals are also very similar in the pressure range covered by the present measurements.

The results of the least-squares fits for the reduced data sets of our measurements at ambient conditions as well as under pressure are summarized in Table II. The table shows the parameter values for ambient pressure and 8 GPa together with the relative decreases, Δ. The estimated uncertainties (in brackets) reflect only the statistical errors in the fitting procedure for all other parameters fixed.

Effects from parameter correlations as well as systematical errors due to limitations of the data sets and truncations in the Hamiltonian can only be estimated. However, a comparison of the data in Table I with the corresponding data in Table II shows that these (systematic) uncertainties may not affect the pressure shifts significantly.

First of all, one can notice that the pressure shifts for all the parameters are the same for Nd^{3+} in the two different host materials. In contrast with this observation, for Pr^{3+} in the two different hosts this seems at first not to be the case. However, one has to keep in mind that the least-squares fits used, instead of the Slater parameters, the Racah parameters, which are linear combinations of the Slater parameters. In these terms the triplet states of Pr^{3+} depend only on E^0 and E^3. In the case of $PrCl_3$ no singlet level of Pr^{3+} could be measured and thus the other two parameters E^1 and E^2 are only determinable via their spin-orbit interaction with the triplets. In this way the results from Pr^{3+}:$PrCl_3$ are not as well established as in the other cases.

To test the sensitivity of the variation of the Slater parameters on the choice of energy levels, a least-squares fit for Pr^{3+}:$LaCl_3$ with the same data set as for Pr^{3+}:$PrCl_3$ was made. In this case the parameters F^2 and F^6 increase with pressure, indicating that the uncertainties in the evaluation of the data for Pr^{3+}:$PrCl_3$ are significantly larger than in the other cases due to the very small data set and missing singlet states.

Comparison of the two ions Pr^{3+} and Nd^{3+} in $LaCl_3$ shows that the change of the spin-orbit-coupling parameter is the same for both ions. In contrast to this result, the variation of the Slater parameters for Pr^{3+} is twice as strong as for Nd^{3+}, explaining the two times larger energy shifts of Pr^{3+} compared to Nd^{3+}.

C. Crystal-field parameters under pressure

In contrast to earlier work[1,2] the present study takes into account effects of J mixing in the evaluation of the crystal-field parameters. This leads to a decrease of the standard deviation from 9.0 to 5.5 cm^{-1} for Pr^{3+} and from 9.3 to 8.9 cm^{-1} for Nd^{3+} at ambient pressure. Without J mixing the standard deviation would increase under pressure to 12 and 13 cm^{-1} for Pr^{3+} and Nd^{3+}, respectively. If J mixing is taken into account the standard deviation remains nearly constant up to 8 GPa. Nevertheless, the general variation of the crystal-field parameters under pressure is not affected very much by the effects from J mixing.

Due to the change of the free-ion parameters, the free-ion eigenvectors also change under pressure. Therefore, in the intermediate coupling scheme one has to calculate the crystal-field reduced matrix elements at each pressure. However, because the influence of this change on the crystal-field parameters is less than 0.5%, the reduced matrix elements calculated with the parameter values at ambient pressure have been used in all least-squares fits.

Figures 5(a) and 5(b) show the variation of crystal-field parameters of Pr^{3+} and Nd^{3+} under pressure. The remarkable similarity of the results for Pr^{3+} and Nd^{3+} in spite of the completely different energy-level schemes and different pressure dependence of the energy levels in both

TABLE II. Free-ion parameters (in cm^{-1}) for Nd^{3+} and Pr^{3+} in different hosts at ambient and high pressure and relative changes Δ. The statistical uncertainties in ( ) result from the complete fit of free-ion and crystal-field parameters using a total of N energy levels, respectively.

	Nd^{3+}:$LaCl_3$			Nd^{3+}:$NdCl_3$		
Parameter	0 GPa	8 GPa	Δ(%)	0 GPa	8 GPa	Δ(%)
E_{ave}	24 178 (4)	24 072 (4)	−0.4 (1)	24 157 (4)	24 039 (4)	−0.5 (1)
F^2	71 925 (20)	71 442 (21)	−0.7 (1)	71 815 (16)	71 293 (17)	−0.7 (1)
F^4	52 168 (46)	51 994 (50)	−0.3 (2)	52 252 (37)	52 045 (39)	−0.4 (2)
F^6	35 502 (25)	35 344 (27)	−0.4 (1)	35 478 (18)	35 367 (19)	−0.3 (1)
ζ	876.2 (5)	872.3 (6)	−0.4 (1)	872.3 (5)	869.6 (5)	−0.3 (1)
N	30	30		16	16	
	Pr^{3+}:$LaCl_3$			Pr^{3+}:$PrCl_3$		
E_{ave}	9932 (3)	9876 (4)	−0.6 (1)	10 067 (12)	9974 (13)	−0.9 (3)
F^2	68 399 (16)	67 661 (16)	−1.1 (1)	70 722 (155)	69 293 (149)	−2.0 (4)
F^4	50 173 (40)	49 777 (40)	−0.8 (2)	40 152 (388)	50 053 (374)	−0.2 (15)
F^6	32 909 (35)	32 602 (35)	−0.9 (2)	37 297 (321)	35 824 (309)	−3.9 (17)
ζ	746.3 (4)	742.9 (4)	−0.4 (1)	749.1 (3)	745.1 (3)	−0.5 (1)
N	29	29		12	12	

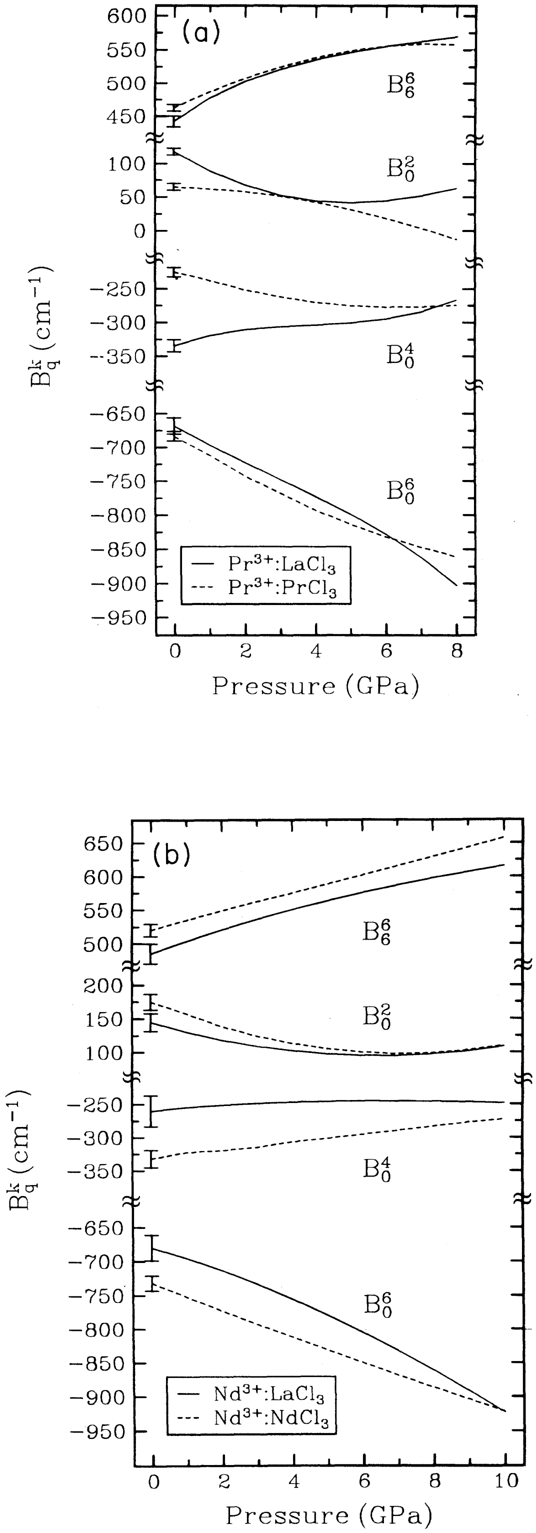

FIG. 5. (a) Variation of crystal-field parameters of Pr^{3+}:$LnCl_3$ under pressure. Error bars represent the statistical errors only. The absolute uncertainties are discussed in the text. (b) Variation of crystal-field parameters of Nd^{3+}:$LnCl_3$ under pressure. Error bars represent the statistical errors only. The absolute uncertainties are discussed in the text.

cases may be noted. The common characteristics of the crystal-field parameters in Figs. 5(a) and 5(b) are as follows. (a) B^6_6 and B^6_0 both show strong increases in their absolute values with pressure, (b) B^4_0 decreases in its absolute value, and (c) B^2_0 may be characterized by a minimum between 5 and 7 GPa.

Larger differences are observed only in the case of Pr^{3+}:$PrCl_3$ for B^2_0 and B^4_0 with respect to all the other results. As previously mentioned, the pressure variation of two levels of Pr^{3+}:$PrCl_3$ seems to deviate from the variation of the same levels of Pr^{3+}:$LaCl_3$. Because the pressure dependences of these two levels may not be well established, least-squares fits with the data of Pr^{3+}:$PrCl_3$ were made, replacing the pressure variation of the uncertain levels by the variation of Pr^{3+}:$LaCl_3$.

While B^6_6 and B^6_0 are not affected by this procedure, B^2_0 and B^4_0 exhibit drastic changes in their pressure variations. Therefore the results for B^2_0 and B^4_0 of Pr^{3+}:$PrCl_3$ are considered to be affected by larger systematic errors and the error bars in Fig. 5(a), showing only the statistical errors, should be about five times larger in the case of Pr^{3+}:$PrCl_3$. Because of these uncertainties more energy levels of Pr^{3+}:$PrCl_3$ are required to be sure about the variation of the crystal-field parameters.

VI. SUPERPOSITION MODEL

In the superposition model[22] the crystal-field parameters B^k_q are separated into radial $\bar{B}_k(R_N)$ and angular $K_{kq}(\Theta_N,\Phi_N)$ parts,

$$B^k_q=\sum_N \bar{B}_k(R_N)K_{kq}(\Theta_N,\Phi_N)\alpha_{k0}/\alpha_{kq} ,$$

where N is the number of ions in the first coordination shell with the spherical coordinates R_N, Θ_N, and Φ_N. The coefficients α_{kq} are given in Ref. 22. The $\bar{B}_k(R)$ are usually referred to as intrinsic crystal-field parameters. Because the superposition model makes no assumptions about the nature of the crystal fields, many different interactions can contribute to the intrinsic parameters. The distance dependence of these parameters should therefore reflect all the effects from the various contributions to the crystal fields. A convenient way to express the distance dependence of the intrinsic parameters is the assumption of a power-law dependence,

$$\bar{B}_k(R)=\bar{B}_k(R_0)(R_0/R)^{t_k} ,$$

where R_0 is an arbitrarily fixed ligand distance and t_k is a fitted parameter. Throughout this work a value of $R_0=2.95$ Å has been adopted. The exact knowledge of the variation of the structural parameters under pressure is essential to perform the superposition model analysis of the crystal-field parameters.

In contrast to the case of the pure samples, one also has to take into account the local distortions around the impurity ions in the doped samples. A method to estimate these distortions for Pr^{3+}:$LaCl_3$ from the optical and structural data of the pure and doped samples has been described in detail.[1] The local distortions around Nd^{3+} in $LaCl_3$ are estimated in the same way in the present work, with the result that R_A decreases by 5.2 ppm and Θ increases by 0.69° around the Nd^{3+} sites, but R_E and δ are not affected. It is assumed that these distortions do not change under pressure. The results for the crystal-field parameters in terms of the superposition model, taking into account the local distortions are shown in Table III. Within the estimated uncertainties, the table shows the excellent agreement for the fitted parameters $\bar{B}_6(R_0)$ and t_6, both for Pr^{3+} and Nd^{3+} substituted either in $LaCl_3$ or in the pure crystals. The average values are for $\bar{B}_6(R_0)=280(31)\ \mathrm{cm}^{-1}$ and $t_6=5.5(20)$.

In the case of $\bar{B}_4(R)$ one finds reasonable agreement in the results for Pr^{3+}:$LaCl_3$ and Nd^{3+}:$NdCl_3$. In the case of Pr^{3+}:$PrCl_3$ the intrinsic parameter $\bar{B}_4$ was not determined due to the above-mentioned uncertainties of the crystal-field parameter B_0^4. With the local distortions of Nd^{3+}:$LaCl_3$ estimated above $\bar{B}_4(R_0)=258(28)\ \mathrm{cm}^{-1}$ and $t_4=-4(2)$ were obtained. The value for the intrinsic parameter at $R_0=295$ pm is comparable to the other cases. Nevertheless the anomalous negative value for t_4 may point either to a failure of the superposition model or to an error due to the assumption of constant local distortions around Nd^{3+} in $LaCl_3$.

In fact, the coordination factor of $\bar{B}_4(R)$ is very sensitive with respect to Θ. Therefore, different variations of Θ under pressure were used. As a result the exponent changes to a value of 4 (listed in Table III) if one assumes a nearly constant angle Θ. However, the intrinsic parameter $\bar{B}_6(R)$ is not affected by this different variation of Θ.

In comparison to the present experimental results *ab initio* calculations of $\bar{B}_6(R)$ by Newman and Ng[23] for Pr^{3+}:$PrCl_3$ yield $\bar{B}_6(R_0)=148\ \mathrm{cm}^{-1}$ and $t_6=10.9$. Thus the experimental value for $\bar{B}_6(R_0)$ is about two times larger than the calculated value whereas the experimental value for t_6 gives only about half of the theoretical value. Other experimental data[24] derived from the comparison of lanthanide ions in $LaCl_3$ and Cs_2NaYCl_6 yield $\bar{B}_6(R_0)=272\ \mathrm{cm}^{-1}$ and $t_6=6$ for Pr^{3+} and $\bar{B}_6(R_0)=288\ \mathrm{cm}^{-1}$ and $t_6=7$ for Nd^{3+}, in close agreement with the present results. For $\bar{B}_4(R)$, Newman and Ng[23] derived $\bar{B}_4(R_0)=162\ \mathrm{cm}^{-1}$ and $t_4=10.7$. As in the case of $\bar{B}_6(R)$, the theoretical $\bar{B}_4(R_0)$ is too small and t_4 too large. The experimental values from Reid and Richardson[24] yield $\bar{B}_4(R_0)=320\ \mathrm{cm}^{-1}$ and $t_4=16$ for Pr^{3+} and $\bar{B}_4(R_0)=320\ \mathrm{cm}^{-1}$ and $t_4=13$ for Nd^{3+}.

TABLE III. Intrinsic parameters (in cm^{-1}).

	$\bar{B}_6(R_0)$	t_6
Nd^{3+}:$LaCl_3$	282 (32)	6 (2)
Nd^{3+}:$NdCl_3$	288 (31)	5 (2)
Pr^{3+}:$LaCl_3$	267 (28)	6 (2)
Pr^{3+}:$PrCl_3$	282 (32)	5 (2)
	$\bar{B}_4(R_0)$	t_4
Nd^{3+}:$LaCl_3$[a]	196 (28)	4 (2)
Nd^{3+}:$NdCl_3$	242 (27)	6 (2)
Pr^{3+}:$LaCl_3$	235 (18)	8 (2)

[a] In contrast to all other cases, the asterisk denotes the use of a nearly constant angle Θ up to 8 GPa.

VII. CONCLUSIONS

The present experimental study of the energy levels for Nd^{3+}:$LaCl_3$, $NdCl_3$ and Pr^{3+}:$LaCl_3$ under pressure shows first of all that the change in the Slater parameters for Pr^{3+} is twice as large as for Nd^{3+}. The variation of the spin-orbit-coupling parameters is the same for both ions under pressure.

The pressure dependences of the crystal-field parameters are similar in all cases. The evaluation of the crystal-field parameters in terms of the superposition model yields values for $\bar{B}_6(R_0)$ and t_6, which are independent of the host material and the impurity ion. For rank 4 parameters, a unified description can be found for Pr^{3+}:$LaCl_3$ and Nd^{3+}:$NdCl_3$. For Nd^{3+}:$LaCl_3$ reasonable agreement is obtained only if a nearly constant angle Θ up to 8 GPa is assumed.

Further studies with different lanthanides in the same host crystals would be useful to support the present observations. Also, an extension of pressure regions would be very interesting if other host materials without structural phase transitions could be found.

ACKNOWLEDGMENT

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) under Grant No. Ho486/14-2.

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