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OF THE CRYSTAL FIELD PARAMETERS
FOR Pr^{3+} IN LaF_3
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*Laboratory of Neutron Physics
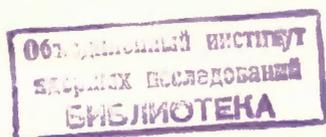
Маттхиз З., Вельш Д.   E14 - 8293

Определение параметров кристаллического поля для
Pr^{+3}: $La F_3$ методом подгонки

Приведены результаты подгонки 23 параметров, включающих параметры кристаллического поля, а также параметры гамильтониана свободного иона, по энергиям электронных уровней Pr^{3+} в кристаллах LaF_3 . Учтены эффекты второго порядка, приводящие к смешиванию состояний с различными J. Сравнением полученных из расчетов энергий и собственных функций состояний с результатами экспериментов по неупругому рассеянию нейтронов установлено, что найденные параметры кристаллического поля достаточно хорошо описывают физические свойства состояний Pr^{3+} в LaF_3.

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Determination of the Crystal Field
Parameters for Pr^{3+} in LaF_3 from
Least-Squares Fits

The results of least-squares fits of the energy levels of Pr^{3+} in crystalline LaF_3 are reported. Especially, by carrying out a 23-variable fit involving the crystal field parameters as well as free-ion parameters second-order effects due to J -mixing are taken into account. From testing the resulting energies and eigenfunctions by inelastic neutron scattering experiments the reported crystal field parameters are expected to describe the physics of Pr^{3+} in LaF_3 sufficiently well.

1. Introduction

In the last years a series of optical investigations on the crystal field-splitted $(4f)^2$ energy levels of Pr^{3+} placed in crystalline LaF_3 has been published [1-4]. By assuming C_{2v} symmetry of the Pr^{3+} ion site in the LaF_3 crystal and using the selection rules for optical transitions Wong et al. [1] suggested a classification of the crystal field levels found experimentally. Except for this attempt a detailed theoretical analysis of the experimental energy-level scheme of $Pr : LaF_3$ does not exist until now. Especially such an analysis should lead to predictions on the crystal field acting on the Pr^{3+} ion. Therefore the main purpose of this paper is to give a detailed account of an approach to this problem where not only the optical data mentioned above but also recent results of inelastic neutron scattering by the crystal field levels of PrF_3 [5] will be used.

2. Fundamental Aspects of the Theory

The Hamiltonian for a $(4f)^n$ lanthanide ion in a crystal lattice can be written as a sum of two parts,

$$H = H_{fi} + H_{cf} , \qquad (1)$$

where H_{fi} is the Hamiltonian for the free ion and H_{cf} is the electrostatic crystal field (ECF) potential [6]. As is well known, the free-ion Hamiltonian H_{fi} , which contains all different interactions of the electrons in the isolated

ion, leads to open-shell 4f–eigenstates that can be described, in general, in terms of $(2J+1)$ -fold degenerated $^{2S+1}L_J$ multiplets with J as the total angular momentum of the n 4f– electrons. L and S mean, respectively, the effective total orbital momentum and effective total spin of the 4f– electrons. These $(2J+1)$-fold degeneracies of the various multiplet levels of the isolated lanthanide ion are either partially or totally removed by the crystal field potential H_{cf} depending on the symmetry of the rare-earth ion site in the crystal. The ECF potential H_{cf} is usually written [7] in terms of a set of real ECF parameters A_m^ℓ as follows:

$$H_{cf} = \sum_{i=1}^{n} \sum_{\ell=2,4,6} \sum_{m=-\ell}^{+\ell} A_m^\ell \bar{Y}_{\ell m}(\Omega_i), \qquad (2)$$

where the (real) $\bar{Y}_{\ell m}(\Omega)$ are the so-called tesseral harmonics [7] related to the usual spherical harmonics $Y_{\ell m}(\Omega)$ [8] by the definition

$$\bar{Y}_{\ell m}(\Omega) = \epsilon_m \{ Y_{\ell-|m|}(\Omega) + \eta_m (-1)^m Y_{\ell|m|}(\Omega) \} \qquad (3)$$

with

$$\epsilon_m = \begin{cases} 1/\sqrt{2} \\ 1 \\ i/\sqrt{2} \end{cases}, \quad \eta_m = \begin{cases} +1 & m > 0 \\ 0 & \text{for} \quad m = 0 \\ -1 & m < 0 \end{cases}.$$

The invariance of H_{cf} under all symmetry operations of the given point group of symmetry of the rare-earth ion site in the crystal can be used to reduce the number of non-zero ECF parameters A_m^ℓ if suitably orientated axes are chosen. Note that the number of non-zero ECF parameters increases when the ion site symmetry is lowered. So, in the case of C_2 (respectively, C_s) symmetry of the Pr^{3+} ion site in crystalline LaF_3 we must take into account fifteen non-zero ECF parameters A_m^ℓ ($\ell=2, m=0,\pm2$; $\ell=4$, $m=0, \pm2, \pm4$; $\ell=6$, $m=0, \pm2, \pm4, \pm6$).

By treating H_{cf} as a perturbation on the various dege-

nerate multiplet levels and states of the free-ion part H_{fi} of the total Hamiltonian the crystal field energy levels can be found in the first-order expansion by diagonalizing appropriate $(2J+1)\times(2J+1)$ matrices. As is known, this procedure leaves the multiplet centers of gravity unchanged. On the other hand, a downward shift in energy of the multiplet centers of gravity relative to the observed gaseous free ion multiplet levels has been found experimentally by many authors [1,9,10]. This effect cannot be explained sufficiently well by only including into the theory higher-order perturbation expansions describing mixing by the crystal field potential of the different J -value states and subsequent shifts of the centers of gravity of the multiplets. That is, the electron shells of a gaseous free ion are deformed when the ion is placed in a crystal lattice and therefore our "free"-ion Hamiltonian H_{fi} is found to differ from the Hamiltonian for the "exact" (gaseous) free ion.

Because of the difficulties connected with the exact solution of the free-ion problem the Hamiltonian H_{fi} is usually handled by using also a parametrization approach. This means, H_{fi} is written within the reduced $|(4f)^n \tau SLJM\rangle$ basis where the various radial integrals corresponding to the different free-ion electron interactions are treated as a set of variable parameters $\{P_{fi}\}$. The parametrization of the electron interactions that must be included into H_{fi} and the structure of the matrix elements of the free-ion Hamiltonian within the above reduced basis set are described in detail in [6,11,12]. For the investigations presented in this paper we have included into H_{fi} Coulombic repulsion interaction between the 4f-electrons (parameters F_2, F_4, F_6), their spin-orbit interaction (parameter ζ), configuration interaction and orbit-orbit interaction of the 4f– electrons (parameters α, β, γ), their spin-other-orbit and spin-spin interactions (parameters M^0, M^2, M^4) [11].

Therefore the total Hamiltonian $H = H_{fi} + H_{cf}$ is found to contain a set of eight free-ion parameters $\{P_{fi}\} = F_2, F_4, F_6, \zeta, \alpha, \beta, \gamma, M^0$ (with the approximation $M^0 = M^2 = M^4$ for the Marvin integrals M^k [13–15]) in addi-

tion to the ECF parameters A_m^ℓ . To determine all these parameters the most convenient way is to fit them to the observed energy-level structure of the given rare-earth ion. In this connection is should be emphasized that because of somewhat different Hamiltonians for the "free" ion in the crystal and the gaseous free ion and due to the fact that the centers of gravity of most of the reported rare-earth multiplets as determined from experimental crystal studies are shifted centers of gravity due to second-order J -mixing both the ECF parameters and the free-ion parameters should be fitted immediately to the ECF splitted multiplet structure problem by including a large number of crystal field levels. Especially in the case of low site symmetry of the lanthanide ion, from the the mathematical point of view, a large number of crystal field levels is needed.

In the following analysis of Pr^{3+} in crystalline LaF_3 we will subdivide the determination of the above fit parameters into three steps:

(i) At the first stage the free-ion parameters $\{P_{fi}\}$ are determined in fitting the eigenvalues of the matrix

$$<(4f)^2 L'S'J'M'|H_{fi}|(4f)^2 LSJM>=\delta_{JJ'}\delta_{MM'}((4f)^2 L'S'J||H_{fi}||(4f)^2 LSJ)$$

to the centers of gravity of the observed ECF energy levels of the various $(4f)^2$ multiplets.

(ii) At the next stage the ECF parameters A_m^ℓ are determined in fitting the eigenvalues of each " $(4f)^2$ multiplet matrix" $<(4f)^2 L_{eff}S_{eff}JM'|H_{cf}|(4f)^2 L_{eff}S_{eff}JM>$, the basis functions

$$|(4f)^2 L_{eff}S_{eff}JM>= \sum_{L,S} C(L,S;L_{eff},S_{eff};J)|(4f)^2 LSJM>$$

resulting from (i), to the relative ECF energy-level positions of the multiplet considered where the relative positions (calculated from the absolute positions observed) refer to the multiplet center of gravity.

(iii) At the last step the free-ion and ECF parameters calculated approximately from (i) and (ii) are used as starting point to determine them more accurately in fit-

ting the eigenvalues of the total Hamiltonian $H=H_{fi}+H_{cf}$ (within the reduced $|(4f)^2 LSJM>$ basis set) to the absolute positions of the crystal field energy levels found experimentally. Hence, the second-order mixing of the different J -values states is expected to be taken into account automatically.

If the ECF energy-level structure of the lanthanide ion is known sufficiently well the above programme, in general, can be realized completely. Otherwise, one must restrict oneself to a fitting scheme more simplified. It should be emphasized that the eigenfunctions deduced from such a reduced fitting approach can be incorrect (with regard to physical effects dominated by the wave-functions) although the calculated energy-level structure is found to be in good agreement with experimental one.

3. The Crystal Structure of LaF_3

Although the first x-ray investigations have been published in 1929 [16] and since that time the LaF_3-type structure has been often the subject of x-ray analysis, EPR and NMR investigations (the latest NMR results have been published by Afanasiev et al. [17] in 1972), optical spectroscopy, neutron diffraction experiments and of other methods, it has not become clear until now (for details see the review article of Sharma [18]).

From the above investigations a series of LaF_3-type structures differing by small displacements of the positions of the La and F ions has been proposed: $D_{6h}^3 (C_{2v})$ [16], $D_{6h}^4(D_{3h})$ [19], $D_{3d}^4(C_2)$ [20-22], $C_{6v}^3(C_s)$ [23,24] (the corresponding site symmetries of the La ions are included in parenthesis). Moreover, there are some facts indicating the possibility of a $D_{6h}^4 - D_{6h}^3$ [25,26], respectively, $D_{6h}^3 - D_{3d}^4$ He -temperature structural phase transition explained by a "freezing" at low temperatures of the statistical motion of the La ions. Similar arguments with regard to the fluorine ions have been used by Afanasiev et al. [17] . From their NMR investigations on PrF_3 they have proposed a crystal structure within the space

group D_{6h}^3 where only six F ions are situated in fixed unit cell locations. The remaining twelve fluorine ions are suggested to be distributed statistically among 24 possible positions. Hence a C_{2v} point symmetry of each Pr ion can be expected at high temperatures only ($\approx 300°K$) but it is not clear what symmetry is at low temperatures. Especially, there is also a fluorine ion distribution with C_2 symmetry of each Pr ion site.

In the present paper we base our investigations of the crystal field problem of Pr^{3+} in LaF_3 on the assumption of C_2 (respectively, C_s) site symmetry of the Pr ion. In view of the used fitting approach to this problem and of the results found by us and from a careful selection among the symmetry variants mentioned above, in our opinion, the assumption of the lowest site symmetry seems to be most justified.

4. Determination of the Free-Ion and ECF Parameters

In this section we will give a detailed analysis of the parameter fit carried out by us for Pr^{3+} in crystalline LaF_3 .

We have based our calculations on the observed energy-level scheme reported by Carnall et al.[3] Only the $^3H_5$ multiplet levels and one $^3H_6$ level (4219 cm^{-1}) have been taken from the data given by Caspers et al.[2] On the whole, there are 13 multiplets that can be derived from the $(4f)^2$ configuration of Pr^{3+}: $^1S_0$, $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^3F_4$, $^3F_3$, $^3F_2$, $^1G_4$, $^3H_6$, $^3H_5$, $^3H_4$, $^1I_6$. Because the $(2J+1)$-fold degeneracies of these multiplets are totally removed by the crystalline potential H_{cf} we find 91 crystal field energy levels. With the exception of the $^1I_6$ and $^3P_1$ multiplet levels all observed energies can be identified unambiguosly with respect to the multiplets mentioned above. Apart from the fact that the ECF level structure of the $^1I_6$ and $^3P_1$ multiplets is available only in part, the energy values known cannot be labelled unambiguously in the above sense because of multiplet overlapping. Therefore we have omitted them out of the energy levels used for the fitting procedure.

We begin with the determination of the free-ion parameters $\{P_{fi}\}$ (stage (i) of the fitting scheme developed in Section 2.). Table 1 (first row) shows the parameter set resulting from the eight-variable fit carried out by Matthies[12]. The mean square deviation of the calculated from the observed multiplet centers of gravity is given by $\Delta E = 17$ cm^{-1} . Similar results have been reported already by Wensky et al. [11]. We emphasize that they are accurate only in part, as has been shown by Matthies [12] .

Before dealing with the second stage of our programme we have to determine suitable starting-point parameters A_m^ℓ and, as far as possible, criteria which enable us to decide whether or not the final parameter set is correct. Especially, when a large number of ECF parameters must be taken into consideration (this takes place in the case of low site symmetry of the rare-earth ion) the success of a parameter fit essentially depends on the carefulness of making choice of the starting-point parameter set. As is known, the parameter determination by fitting the calculated to the observed energy levels is to find the minimum of the function

$$\chi^2 = \sum_i (E_i - E_i^{exp})^2$$

(E_i^{exp} and E_i are, respectively, the observed and the calculated energies, the latter depending on the fit parameters). If the number of fit parameters is sufficiently large and, in addition, the starting-point parameter set is far off the true set the attempt of selecting the "physical" minimum among other ones can be expected to be nearly hopeless [6]. Even by the aid of additional selection criteria, which should be available (in cases such as Pr^{3+} in LaF_3 where we are dealing with 15 ECF parameters) for overdetermining the parameters by other than energy data, this difficulty cannnot be removed. [1]

As is noted in the introduction, Wong et al. have suggested an identification in terms of the C_{2v} group

Table 1. Best free-ion fit parameters for Pr^{3+} in crystalline LaF_3 (units in cm^{-1})

	F_2	F_4	F_6	ζ	α	β	γ	M°
(i)	306.021	46.4008	4.44628	749.546	15.21846	-710.239	1453.27	0.399306
(iii)	306.454	46.4150	4.46133	749.206	16.4467	-633.463	1446.47	1.22304

(i)   8-variable fit (without second-order J-mixing)
(iii) 23-variable fit (with second-order J-mixing)

representation labels of the observed ECF energy levels of Pr^{3+} in LaF_3 basing the investigations on group theoretical selection rules for optical E1-transitions with polarized light. Although from their classification scheme most observed spectral lines are explained sufficiently well there are some weak lines that should be forbidden. These and other obscurities (for example, the proposed classification is unambiguous only in part) can be removed by assuming a lower site symmetry of the Pr ion (e.g., C_2 symmetry). In particular, let us consider the ground state multiplet $^3H_4$. Its ECF level classifications for C_{2v} symmetry (labels Γ_i') and C_2 symmetry (labels Γ_i) are related to one another as follows

$$\Gamma_1' \to \Gamma_1 , \quad \Gamma_2' \to \Gamma_2 , \quad \Gamma_3' \to \Gamma_1 , \quad \Gamma_4' \to \Gamma_2$$

(see, for example, Heine's book on group theory[27]). Assuming C_2 symmetry and choosing the coordinate system used by Wong et al.[1] (where the y -axis is chosen to be parallel to the C -axis of the hexagonal unit cell) we get the following selection rules for E1-transitions with polarized light (the direction of π -polarization is parallel to the C -axis):

	Γ_1	Γ_2
Γ_1	σ	π , σ
Γ_2	π , σ	σ

The energy-level classification which is in consistence with these selection rules is shown in Table 2 (third column). It is one of the criteria used below for proving the correctness of the resulting ECF fit parameters. From Table 2, in particular, the ground state is expected to be a Γ_1 -level. This is also affirmed by the investigations of Onopko[28] who has determined the ECF parameters for Ce^{3+}, Nd^{3+}, Er^{3+} in crystalline LaF_3 by assuming D_{3h} site symmetry. Interpolating the A_m^ℓ -values of Pr^{3+} from the reported

Table 2. The experimental and calculated energy-level schemes of the $^3H_4$ multiplet of Pr^{3+} in crystalline LaF_3 (units in cm^{-1})

No	Experimental values		Ab initio values				Best fit values			
			C_2 site symmetry		C_s site symmetry		(ii)		(iii)	
9	508	Γ_1	547	Γ_2	566	Γ_2	498	Γ_1	498	Γ_1
8	322	Γ_1	494	Γ_2	493	Γ_1	397	Γ_2	409	Γ_2
7	296	Γ_1	415	Γ_1	406	Γ_2	354	Γ_1	336	Γ_1
6	204	Γ_1	279	Γ_2	268	Γ_2	259	Γ_1	243	Γ_1
5	295	Γ_2	264	Γ_1	222	Γ_1	253	Γ_2	204	Γ_2
4	136	Γ_1	233	Γ_2	219	Γ_1	178	Γ_2	177	Γ_2
3	76	Γ_1	145	Γ_1	176	Γ_1	110	Γ_1	107	Γ_1
2	57	Γ_2	133	Γ_2	71	Γ_2	94	Γ_1	79	Γ_2
1	0	Γ_1	0	Γ_1	0	Γ_1	0	Γ_1	0	Γ_1

(ii)   15-variable fit (without second-order J-mixing)

(iii)   23-variable fit (with second-order J-mixing)

values for Ce^{3+} and Nd^{3+} and going to C_{2v}, respectively, C_2 symmetry we find the ground state of Pr^{3+} to be a Γ_1 -level.

The simplest ab initio method for calculating ECF parameters is based on the electrostatic point-charge model [7]. Since this model has often led to serious disagreements with the empirical parameter values it seems not very advantageous [6] to derive the starting-point parameters from the use of it. Therefore we have employed the theory developed by Newman and coworkers which have taken into account electrostatic contributions as well as many-electron ones to the ECF parameters (see the review article of Newman [29] and references therein). Within the framework of their superposition model [29] A_m^ℓ can be written as

$$A_m^\ell = \sum_j \bar{k}_{\ell m}(\Omega_j) \bar{A}_\ell(R_j), \qquad (4)$$

where the "structural" factors $\bar{k}_{\ell m}(\Omega_j)$ and "intrinsic" parameters $\bar{A}_\ell(R_j)$ depend, respectively, on the angular coordinates Ω_j and the radial positions R_j of the ions

(enumerated by the index j) surrounding the rare-earth ion (which is situated at the origin of the coordinate system) and the summation is taken over all ions that contribute to the ECF parameters significantly. In practice this summation is often restricted to those terms which arise from the nearest-neighbouring ligands. We emphasize that the structural factors are only determined by the geometry of the given crystal while the intrinsic parameters must be calculated by quantum-chemical methods (such as the complex model of Newman [29]).

In the special case of Pr : LaF_3 the superposition model corresponds to the assumption that the total crystal field acting on the Pr^{3+} ion can be built up from separate contributions, each arising from a single $Pr^{3+}-F^-$ system. The corresponding intrinsic parameters $\bar{A}_\ell(R)$ as functions of the interionic distance R are given in the article of Newman [29]. We note that the formulae derived in the quoted paper (pp. 209, 210) for calculating the structural factors are inaccurate. They must be corrected as follows: $S_0^4 = 1/8(4\pi/9)^{1/2}$, $(S_2^2/S_0^2)^2 = 3$, $(S_1^6/S_0^6)^2 = 84$. From the above and from the use both of the D_{3d}^4 structural data reported by Mansman [21,22] and of the C_{6v}^3 data given by Andersson et al. [24] we have calculated ECF parameter sets by taking into account 11 nearest F neighbours. Their polar coordinates are given in Table 3 (the axes are chosen as shown in Fig. 1). The resulting parameter sets are reported in Table 4 (columns 2 and 3). We point out the fact that we find two nearest-neighbour arrangements of the fluorine ions (the cases (a) and (b) in Fig. 1 and Table 3) if assuming the crystal structure D_{3d}^4 (site symmetry C_2). The reason is that there are two kinds of La ions (respectively, Pr ions), the F surroundings of which can be transformed into one another by a reflection at the hexagonal $x_h y_h$-plane, provided that a suitable coordination of the two systems considered has been made (see Fig. 1). The two A_m^ℓ -parameter sets realizing the cases (a) and (b) are identical for $m \geq 0$ and differ in sign for $m < 0$. Because this change in sign keeps the secular determinant of the Hamiltonian unchanged both sets lead,
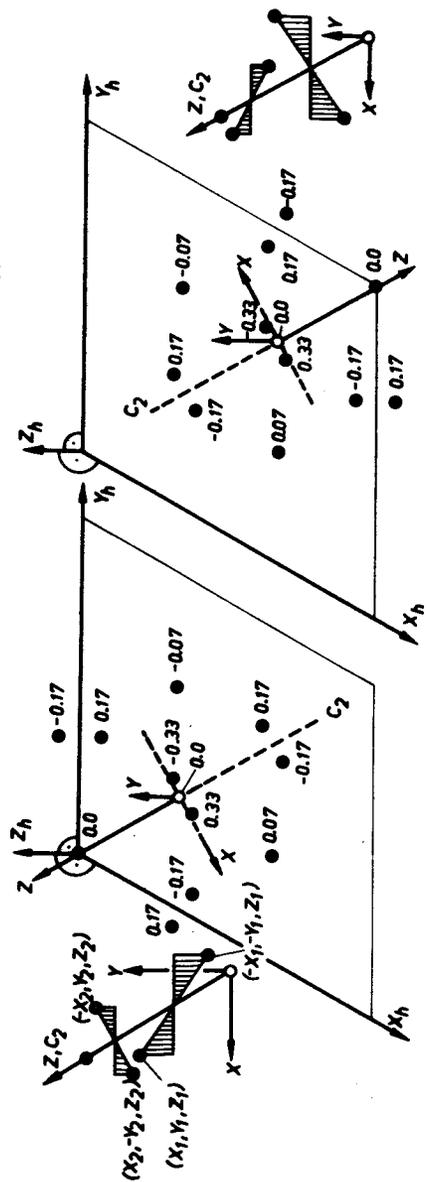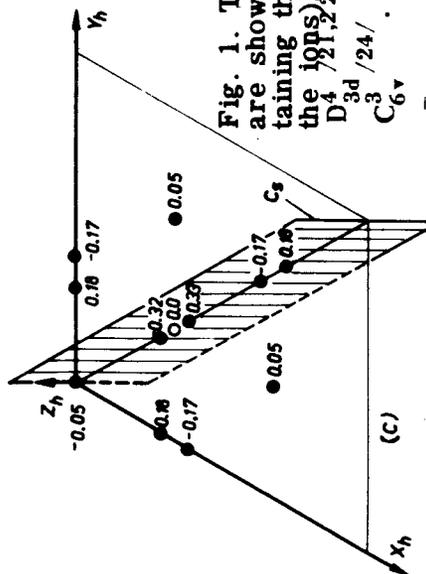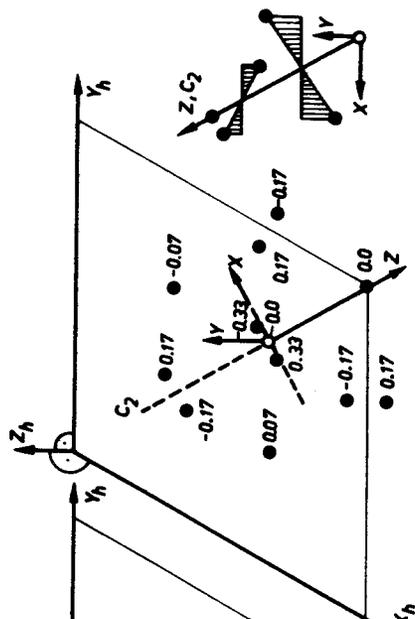
Fig. 1. The nearest F⁻ neighbours (•) of a La³⁺ ion (o) are shown in projection on the hexagonal $x_h y_h$-plane containing the La³⁺ ion(the numbers are the z_h coordinates of the ions)/21,22/.(a), (b) The crystal structure is assumed to be D^4_{3d} /24/ .(c) The crystal structure is assumed to be C^3_{6v}

Table 3. The position of eleven nearest-neighbour F⁻ ions derived L re from the data /21, 22/ for D^4_{3d} structure of LaF₃

Ions	R(Å)	ϑ(deg)	φ(deg) case(a)¹⁾	φ(deg) case(b)¹⁾	φ(deg)/31/
1	2.454	0.0	-	-	-
3(2)²⁾	2.476	69.20	147.52	212.48	147.52
5(4)	2.471	90.56	260.97	99.03	260.97
7(6)	2.607	150.03	107.33	252.67	107.33
9(8)	2.420	118.13	193.47	166.53	166.53
11(10)	3.070	59.66	27.97	332.03	

1) See Fig. 1
2) The positions of the bracketed ions are (R, ϑ, φ + 180°)

Table 4. The ab initio ECF parameters A^l_m and the best fit ones for Pr³⁺ in crystalline LaF₃ (units in cm⁻¹)

l,m	Ab initio values C₂ site symmetry	Ab initio values Cₛ site symmetry	Best fit values (ii)	Best fit values (iii)
2,2	226.027	-151.424	-163.978	-77.1263
4,2	665.062	-666.028	717.763	708.299
4,4	601.366	-946.376	279.932	921.326
6,2	-1377.22	-823.074	-965.072	-1102.40
6,4	85.4206	752.404	327.348	117.430
6,6	-213.999	-647.076	294.302	58.0116
2,0	-13.1244	-85.5169	30.1953	-46.7048
4,0	858.512	703.042	617.801	554.897
6,0	547.801	-1233.65	799.903	731.725
2,-2	48.5437	28.8683	354.607	120.559
4,-2	-396.940	779.290	-43.4586	86.9679
4,-4	-753.403	-551.129	-906.346	-778.478
6,-2	0.0¹⁾	0.0¹⁾	0.0¹⁾	0.0¹⁾
6,-4	787.637	601.022	770.188	719.618
6,-6	1141.97	903.648	695.738	857.848

(ii) 15-variable fit (without second-order J-mixing)
(iii) 23-variable fit (with second-order J-mixing)

1) One of the ECF parameters can be chosen to be zero if the x-axis is suitably oriented /33/.

of course, to the same energy levels. One the other hand, a line-doubling, as observed by Afanasiev et al.[17] and Hadni et al.[30], might be explained, for example, by small lattice deformations, which are suspected to remove the physical equivalence of the cases (a) and (b). Finally we note that the fluorine ions chosen by Stedman and Newman [31] (apart from two errors in the ionic positions reported) correspond to our case (a) (see Table 3).

Starting with the ECF parameter sets calculated above (columns 2 and 3 in Table 4), from the second stage of our fitting scheme we have found the A_m^ℓ- values presented in the fourth column of Table 4. The mean square deviation of the resulting energy levels from the experimental ones is given by 27 cm^{-1}. Except the levels of the multiplets $^1S_0$, $^3P_0$, $^1I_6$, $^3P_1$ we have included into the parameter fit all 73 energy levels of the remaining multiplets. In order to calculate the matrix elements of H_{cf} we have employed the relation

$$< (4f)^2 LSJM \mid \sum_{i=1}^{2} Y_{\ell m}(\Omega_i) \mid (4f)^2 L'S'J'M'> =$$

$$= -14\{(2\ell+1)/4\pi\}^{1/2} (-1)^{M+S+J+J'} \delta_{SS'} \times$$

$$\times \{(2L+1)(2L'+1)(2J+1)(2J'+1)\}^{1/2} \times$$

$$\times \begin{Bmatrix} \ell & L' & L \\ 3 & 3 & 3 \end{Bmatrix} \begin{Bmatrix} \ell & J & J' \\ S & L' & L \end{Bmatrix} \begin{pmatrix} \ell & 3 & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & \ell & J' \\ -M & m & M \end{pmatrix} . \qquad (5)$$

The last step in our analysis is to take into account the second-order mixing by the crystal field potential of the different J-value states. In this sence we have treated at the same time the free-ion parameters $\{P_{fi}\}$ and the ECF parameters A_m^ℓ as free variables to obtain a least-squares fit to 75 absolute crystal field level positions observed (only the levels of the multiplets $^1I_6$ and $^3P_1$ have been excluded from consideration). The expressions for the matrix elements of the free-ion Hamiltonian

Table 5. The $^3H_4$ eigenfunctions resulting from the 23-variable fit (the quoted numbers are the coefficients for expanding the eigenfunctions within the real $|(4f)^2 \ LSJM>_t$ basis derived from the $|(4f)^2 \ LSJM>$ basis by the aid of Eq.3)

$^{2S+1}L_J$	M	$\tilde{J}_2$ levels Level numbers[1]			
		2	4	5	8
$^1D_2$	-1	.20528E-02	-.15347E-02	.83398E-04	-.11353E-02
	1	-.42461E-03	.37771E-03	.68721E-04	.36771E-02
$^1G_4$	-3	-.17827E-01	.11883E+00	-.63029E-01	-.83094E-01
	-1	-.42725E-01	.74973E-01	.13166E+00	-.14409E-01
	1	.10557E+00	.89055E-01	-.40443E-02	.10092E+00
	3	-.10717E+00	.24682E-01	-.33195E-01	.10841E+00
$^1I_6$	-5	-.42242E-03	.62308E-03	-.19909E-02	-.13878E-02
	-3	.11860E-02	-.25072E-02	-.70842E-03	.16586E-03
	-1	.61425E-03	-.56652E-03	-.22338E-02	-.16648E-03
	1	.10735E-02	-.98067E-03	.83306E-03	.41396E-03
	3	.17158E-02	-.95400E-03	.37293E-03	-.38764E-03
	5	-.17928E-02	-.16968E-02	-.23299E-02	.71907E-03
$^3F_2$	-1	.22448E-01	-.15936E-01	.10862E-02	-.11799E-01
	1	.96909E-02	.57868E-02	.41388E-02	.42982E-01
$^3P_2$	-1	.27922E-02	-.19462E-02	.79001E-04	-.13591E-02
	1	.46586E-02	.10168E-02	.14289E-02	.57862E-02
$^3H_4$	-3	-.13429E+00	.71662E+00	-.44641E+00	-.49186E+00
	-1	-.25446E+00	.42715E+00	.84931E+00	-.72515E-01
	1	.63523E+00	.49741E+00	-.12413E-01	.56225E+00
	3	-.69816E+00	.16111E+00	-.23660E+00	.63521E+00
$^3F_4$	-3	-.54518E-02	-.21187E-01	-.97971E-02	.16909E-01
	-1	.94846E-02	-.21240E-01	-.59704E-02	.67655E-02
	1	-.20168E-01	-.28072E-01	.47477E-02	-.30537E-01
	3	.37427E-02	-.46260E-03	-.60246E-02	.24380E-01
$^3H_6$	-5	.73067E-02	-.35015E-02	.10029E-01	.13546E-01
	-3	-.10205E-01	.13273E-01	-.39825E-02	-.54555E-03
	-1	-.33557E-02	.97616E-03	-.14765E-01	.29457E-02
	1	-.40167E-02	.77463E-02	-.54919E-02	-.12612E-02
	3	-.57439E-02	.74928E-02	-.65208E-02	.39646E-02
	%	.99883E-02	.66207E-02	.13793E-01	-.65571E-02

1) For level numbers see Table 2 (first column)

H_{fi} have been taken from [12]. The matrix elements of the ECF Hamiltonian H_{cf} have been calculated from the use of Eq. 5. We have started the 23-variable fit by using the free-ion parameters from stage (i) and the ECF parameters determined from stage (ii) of our fitting concept. Table 1 (second row) shows the resulting free-ion parameters. The corresponding best ECF parameters are given in Table 4 (fifth column). They have been found to describe the 75 absolute level-positions considered within a mean square-error of 29 cm^{-1}.

Table 5 - continued

$2S+1_{L_J}$	M	Γ_4 levels
		Level numbers[1]
		1	3	6	7	9
$^1S_0$	0	-.13210E-02	-.93316E-03	-.12502E-03	-.20704E-03	-.56942E-03
$^1D_2$	-2	.39204E-03	-.70070E-04	-.16580E-02	.27780E-03	-.43587E-03
	0	-.16291E-02	-.15485E-02	.16534E-03	.28541E-02	-.19108E-02
	2	-.17238E-02	-.20437E-02	-.78789E-03	-.17942E-02	.99181E-03
$^1G_4$	-4	-.90454E-01	.23359E-02	.11176E-00	.28192E-01	-.78083E-01
	-2	-.28404E-01	-.34692E-01	.46210E-01	.68690E-01	.14036E+00
	0	.11372E-00	-.58002E-01	.71250E-01	.49021E-01	-.40028E-01
	2	.12447E-01	.11308E+00	-.29220E-01	.11880E+00	-.32661E-01
	4	.48087E-01	.97156E-01	.90015E-01	-.70215E-01	.51520E-01
$^1I_6$	-6	.22116E-02	.96574E-03	-.99283E-03	.14952E-02	-.10033E-02
	-4	.94958E-04	.90622E-03	.52139E-04	.12222E-02	-.28868E-03
	-2	.16535E-02	.99505E-03	-.16712E-02	-.26865E-04	.79901E-03
	0	.62572E-03	-.44387E-03	.18492E-02	-.11027E-02	-.14089E-02
	2	-.13953E-02	-.27643E-02	-.58650E-03	.18567E-03	.39405E-02
	4	-.15749E-02	.88812E-03	-.54799E-03	.83701E-04	.15072E-02
	6	-.57366E-04	-.11494E-02	-.11804E-02	-.93467E-03	-.21488E-02
$^3P_0$	0	-.71125E-02	-.49247E-02	-.58978E-03	-.11426E-02	-.29049E-02
$^3F_2$	-2	-.77314E-03	-.93237E-02	-.16607E-01	.23969E-02	-.76890E-02
	0	-.17401E-01	-.29535E-02	-.71222E-02	.30331E-01	-.16138E-01
	2	-.23454E-02	-.21150E-01	-.12375E-01	-.20553E-01	.82700E-02
$^3P_2$	-2	-.11946E-02	-.31482E-02	-.19007E-02	.26784E-03	-.16216E-02
	0	-.21039E-02	.27420E-02	-.29614E-02	.35537E-02	-.83030E-03
	2	.34201E-02	-.25509E-02	-.24522E-02	-.27418E-02	.41494E-03
$^3H_4$	-4	-.57292E+00	.27549E-02	.66087E+00	.14297E+00	-.42960E+00
	-2	-.18333E+00	-.20001E+00	.26382E+00	.44446E+00	.79281E+00
	0	.72381E+00	-.36767E+00	.40681E+00	.30780E+00	-.23290E+00
	2	.90344E-01	.65791E+00	-.17002E+00	.69114E+00	-.14008E+00
	4	.28381E+00	.60252E+00	.51773E+00	-.42408E+00	.27962E+00
$^3F_4$	-4	.88336E-02	-.37098E-02	-.23682E-01	-.12896E-01	.24865E-01
	-2	.16995E-02	.91413E-02	-.12497E-01	-.31431E-02	-.38767E-01
	0	-.98406E-02	.53101E-02	-.19704E-01	-.49632E-02	.92186E-02
	2	.25617E-02	-.28099E-01	.71035E-02	-.27786E-01	.21360E-01
	4	-.11244E-01	-.12884E-01	-.23529E-01	.12121E-01	-.17491E-01
$^3H_6$	-6	-.13027E-01	-.36285E-02	.32767E-02	-.11739E-01	.46395E-02
	-4	.57683E-02	-.89158E-02	-.19677E-03	-.48164E-02	.39856E-02
	-2	-.10905E-01	-.55288E-02	.11045E-01	.30505E-02	-.21402E-02
	0	-.35115E-02	-.12726E-02	-.11602E-01	-.99967E-02	.81937E-02
	2	.91347E-02	.16598E-01	.41793E-02	-.17428E-02	-.38764E-03
	4	.54145E-02	-.44838E-02	-.24137E-02	.31274E-03	-.10096E-01
	6	-.41613E-03	.39135E-02	.62271E-02	.40961E-02	.11272E-01

Together with the experimental ECF energy values for the ground state multiplet $^3H_4$ and their classification suggested by heuristic reflections, in Table 2 we have summarized the corresponding energy-level schemes and classification schemes calculated from the use both of the ab initio ECF parameters and of the fitted ones. The $^3H_4$ eigenfunctions resulting from the 23-variables fit are presened in Table 5.

All the numbers quoted in this paper have been obtained by using programmes run on computers BESM-6, CDC-1604A, CDC-6200, the matrix diagonalizations being performed by the aid of a special subroutine available in Dubna. In order to get least-squares fits we have developed a computer programme underlying an algorithm proposed by Oehler [32].

5. Conclusion

From Table 2 the energy levels of the ground state multiplet $^3H_4$ and their identification in terms of group representation labels, both calculated from the 15-variable fit and the 23-variable fit (involving the second-order J -mixing), are seen, in general, to be in good agreement with the observed energies and the classification scheme proposed from experimental data. In addition, we have used the eigenfunctions resulting from the 23-variable fit for calculating cross sections for inelastic neutron scattering [5]. Comparison with the experiment shows an excellent agreement [5] so that the choice of the fit parameter sets reported seems to be fully justified.

Although the ab initio ECF parameter set calculated from the assumption of C_2 site symmetry (column 2 in Table 4) leads to an energy-level scheme (columns 4 and 5 in Table 2) which is in a somewhat better agreement with the experimental one than that (columns 6 and 7 in Table 2) derived from the ab initio parameters for C_s site symmetry (column 3 in Table 4) it cannot be decided in favour of one of the crystal structures proposed. The reason is

that both the ab initio sets are found to differ considerably from the final fit parameter sets.

Calculating the multiplet centers of gravity from the use of the two reported fit parameter sets differing by second-order effects (rows 1 and 2 in Table 1 and columns 4 and 5 in Table 4) Matthies [12] has found center shifts differing in about 20 cm $^{-1}$. This is in agreement with the estimations given by Wong and Richman [10].

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