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The anomalous crystal field splittings of $^2H_{11/2}(Nd^{3+}, 4f^3)$

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Résumé. — L'éclatement expérimental de quelques niveaux électroniques d'ions de terres rares s'écarte notablement des valeurs prédites par le calcul. Cela se produit notamment pour le niveau $^2H_{11/2}$ de Nd^{3+} à 16 000 cm^{-1} au-dessus du niveau de base. Le désaccord est tellement systématique et criant qu'on ne peut accuser le procédé d'affinement mais plutôt suspecter une défaillance occasionnelle de la théorie du champ cristallin. L'éclatement expérimental du $^2H_{11/2}$ peut être reproduit en utilisant, pour ce niveau seulement, des valeurs élevées du paramètre de Racah E^2 ou bien des valeurs élevées du paramètre de champ cristallin B_0^2. Mais par ailleurs, l'ordre de grandeur du désaccord entre la simulation et l'expérience est en relation étroite avec le comportement du niveau quand il se couple avec son « jumeau » de même S, L, J, observé vers 35 000 cm^{-1}. Il est suggéré l'existence d'un mécanisme qui découple tous les niveaux jumeaux. Des ajustements de paramètres ion-libre et de champ cristallin sont entrepris avec des jumeaux découplés pour $LiYF_4 : Nd^{3+}$, NdOCl, et $Y_2O_3 : Nd^{3+}$ avec des résultats plutôt satisfaisants.

Abstract. — The experimental splitting of some particular electronic energy levels of trivalent rare earths deviates strongly from predicted values. It happens namely for the $^2H_{11/2}$ level of Nd^{3+} at 16 000 cm^{-1} above the ground state. The disagreement is so systematic and conspicuous whatever the compound that it cannot be assigned to an imperfection of the fitting procedure but rather to a specific failure of crystal field theory. The experimental splitting of the $^2H_{11/2}$ level can be reproduced by utilizing for this level only, high values of Racah's parameter E^2 or high crystal field parameters (B_0^2). But also, it is noteworthy that the magnitude of the discrepancy is strongly related to the behaviour of the level when it is coupled with its « twin », displaying the same S, L, and J values and observed at about 35 000 cm^{-1}. It is proposed that some mechanism uncouples all the twin levels. Refinements of free-ion and crystal field parameters are fulfilled with uncoupled twins for $LiYF_4 : Nd^{3+}$, NdOCl, and $Y_2O_3 : Nd^{3+}$ and yield rather satisfactory results.

Introduction.

The position of the discrete energy levels of the $4f^n$ configurations in solids is, in general, well simulated using an hamiltonian which involves the adjustment of both free atom and crystal field parameters (c.f.p.). The crystal field hamiltonian is usually written in Wybourne's formalism : $H = \sum B_q^k \cdot C_q^k$. A few configurations ($4f^{1,2,3,11,12,13}$) can be treated without

truncations, other ($4f^6$, $4f^7$) have to be truncated, but, on a whole, coherent results are found for the values of the c.f.p. of different lanthanides utilized as crystal field probes in the same site of isomorphous structures.

It is known, however, that the experimental decomposition of levels in some configurations deviates strongly from the predicted calculated values. The experimenters usually discard these levels from the fitting procedure. One of the most famous cases is the $^2H(2)_{11/2}$ level of neodymium $4f^3$, at circa 6 250 Å. It is well isolated and its energy positions are easy to record either by absorption at liquid helium temperature or by the monitoring of the excitation spectrum of the infra-red neodymium luminescence. An experimental spectrum for Nd^{3+} in the C_2 site of C-Y_2O_3 is shown in figure 1. The very large disagreement between experimental and calculated values for this level has been reported by several investigators (Ref. [1-5]). The experimental levels are usually much more widely split than the calculated ones.

The aim of the present paper is to report our efforts to find an effective operator which can fit the observed $^2H(2)_{11/2}$ levels.

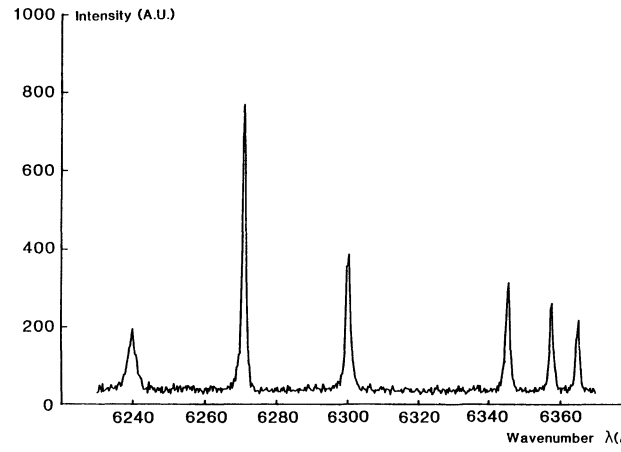

Fig. 1. — The excitation spectrum of the $^2H(2)_{11/2}$ area of the Nd^{3+} (4 %) in Y_2O_3 luminescence at 8 937.2 Å (C. Pedrini, B. Jacquier and G. Boulon).

1. The effect of the variation of free atom parameters.

In a free atom calculation, the $^2H_{11/2}$ level at circa 16 000 cm^{-1} appears as a mixture of the $^2H(2)$ level (v = (210), u = (21)) with the $^2H(1)$ level (v = (210), u = (11)). The former predominates ($\not\approx$ 90 %). This level is consequently a « twin » mainly built out of two components with the same S, L, and J values, the remaining principal component being $^4G_{11/2}$.

The other $^2H_{11/2}$ levels can be observed at circa 34 500 cm^{-1}. This is a rather high value and the crystal field decomposition has only been observed in a few cases namely for $LaCl_3:Nd^{3+}$, NdOCl, NdF_3, $LiYF_4$, and Nd_2O_3. No « abnormal » behaviour has been reported for this level (which means that it roughly agrees with the calculation).

Amid the free ion Racah's parameters, only E^2 is present in the matrix elements between $H(2)$ and $H(1)$. The arbitrary variation of E^2 into an unrealistic domain has a drastic effect on the crystal field decomposition of the lower level as shown by figure 2 drawn for the case of

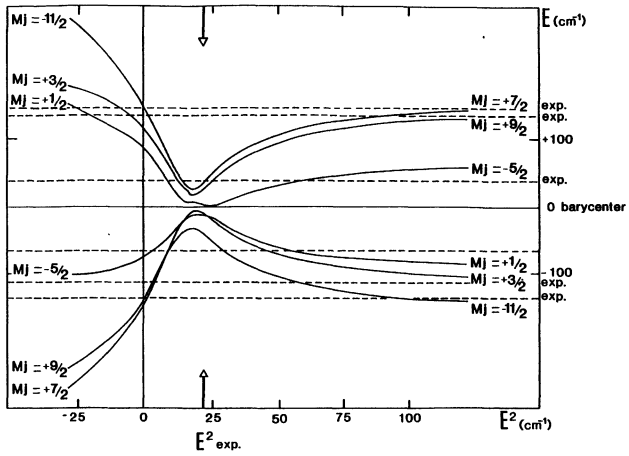

Fig. 2. — A simulation of the $^2H(2)_{11/2}$ (small 24 × 24 matrix) crystal field splitting (Nd_2O_3 crystal field parameters) when the free atom E^2 parameter is varied between unrealistic limits. The M_j value labels the wave vectors. There is a crystal field constriction for the « normal » E^2 value (arrow).

Nd^{3+} in Nd_2O_3. For a « normal » value of E^2 in the $4f^3$ configuration, that is, slightly under 25 cm^{-1}, one observes an obvious constriction of the crystal field decomposition of the level. For this C_{3v} case, the M_j labelling of the levels forbids a crossing of the levels. However, the particular value of E^2 which has to be used to fit free atom levels in the $4f^3$ configuration induces a pseudo degenerate situation under the crystal field (and as a matter of fact for *any* usual c.f.p. values).

An empirical operator is able to lift this pseudo-degeneracy. For instance, it is clear from figure 2 that a very high value of E^2 yields a decomposition which is in fair agreement with the observed results. But also, it is clear that such a large E^2 value is unrealistic and cannot be used in any $4f^3$ calculation.

To work out an empirical operator, two approaches are possible. One of them consists in trying to modify the free atom part of the hamiltonian, keeping the c.f.p. as determined from the other levels. The other consists in keeping the free atom parameters and trying to produce a set of empirical c.f.p. valid for this level alone. Help can be obtained from the effect of the empirical operator on the experimental *versus* calculated behaviour of the $^2H(2)_{11/2}$ levels in the sister $4f^{11}$ configuration of Er^{3+}. It is advisable to seek empirical operators across a rather large number of compounds. By chance, for neodymium, numerous c.f.p. are known with a good precision.

Still, another approach is possible, which lies on the experimental evidence that for each investigated compound, without any exception, the discrepancy (observed/calculated) is correlated with the strength of the interaction with the « twin » term. The observed discrepancy might therefore be caused by the contraction of the lower level, as a consequence of the crystal field interaction between the twin terms. This statement will be examined in Part II hereafter.

The phenomenon is hindered if other levels are significantly involved in the mixing. In Part III, we shall give an example of this behaviour displayed by the $^2H_{11/2}$ levels in Er^{3+}.

The consequence of the statement is that some mechanism might inhibit the crystal field interaction between twins. Therefore, in Part IV, we selected three Nd^{3+} spectra and

endeavoured to adjust all the observed spectral lines including the $^2H_{11/2}$ levels,with the hypothesis that part or all of the crystal field interaction between pairs had disappeared. The agreement experimental/calculated was improved in each case.

At last, we stated that an improvement on the agreement experimental/calculated could also be obtained by utilizing within the lower $^2H_{11/2}$ level, an additionnal operator acting like C_0^2 and associated with a very large parameter (Part V).

2. Correlation between discrepancies and the contraction of the lowest term of a set.

We shall first give further examples of the discrepancy concerning the $^2H_{11/2}$ level of Nd^{3+} for which there exists a number of experimental results from various origins. We have namely investigated the data concerning Nd^{3+} in $LaCl_3$ [6] and $Nd(C_2H_5SO_4)_3 \cdot 9\,H_2O$ [7], $Nd(NO_3)_3 \cdot 6\,H_2O$ [8], NdOCl [9], $NdAlO_3$ [5], NdF_3 [10], Nd_2O_2S [2], $LiYF_4 : Nd^{3+}$ [11], Nd_2O_3 [4], $Y_2O_3 : Nd^{3+}$ [1, 12] and $Y_3Al_5O_{12} : Nd^{3+}$ [13, 14].

The overall splitting of the $^2H(2)_{11/2}$ level increases along this series. In table I, second column, stand the observed experimental overall splittings (ΔE_o) and in column 3, the calculated splittings ΔE_c (resulting from a complete 364×364 matrix diagonalisation) with the c.f.p. given in the cited references. Column 4 gives the $\Delta E_o/\Delta E_c$ ratios which range between 1 for the nitrate (a rather isolated case) and 4.23 (for Nd_2O_2S).

In order to show simply the effect of the coupling with a twin term, without utilizing the complete 364×364 interaction matrix, we have built the small phenomenological interaction matrix, taking into account electrostatic 4f-4f and parametric crystal field effects between the sub-levels of $^2H_{11/2}$ only. The dimension of this matrix is 24×24 and suffices for the present purpose.

For each compound the diagonalization is performed twice, once with the crystal field interaction between the terms switched on, and once without. When mixed up with its twin, the lowest term (in energy) is mainly $^2H(2)$ and the highest one $^2H(1)$.

Figures 3-1, 2, ... 11 represent for each compound the experimental levels, the coupled levels calculated in a 364×364 matrix, and the coupled and uncoupled levels calculated in a 24×24 matrix. It is noteworthy that the $^2H_{11/2}$ levels calculated in the small matrix are quite similar to those coming out of the complete diagonalisation, at least when the splitting is large, in which cases foreign levels have but a small influence on the splittings of the $^2H_{11/2}$ levels.

We report in table I column 5, the overall calculated splitting of the $^2H(2)$ term when isolated (ΔE_i), in column 6 the calculated splitting when it is coupled (ΔE_{co}) and in column 7 the ratio between the splittings of the isolated $^2H(2)$ term and the coupled $^2H(2)$ term $\Delta E_i/\Delta E_{co}$.

The correlation between the values standing in columns 4 and 7, table I is obvious. The higher the contraction of the lowest term, due to the interaction with its twin, the higher the discrepancy between the observed and the calculated splitting. This is shown by figure 4 giving the variation of $\Delta E_o/\Delta E_c$ as a function of $\Delta E_i/\Delta E_{co}$. As a consequence of the statement, it seems that when the discrepancy is large, the only way to match calculated and experimental levels is to uncouple partly or completely the « twin » levels.

We can investigate the separate effects of second, fourth and sixth order parameters on the splitting of coupled and uncoupled levels. Therefore, taking into account the expression for the « strength » of the crystal field derived in reference [15] :

$$\bar{E}^k = \begin{pmatrix} 1 & 1 & k \\ 0 & 0 & 0 \end{pmatrix} |B^k| \left(\frac{21+1}{2k+1} \right)^{1/2};$$

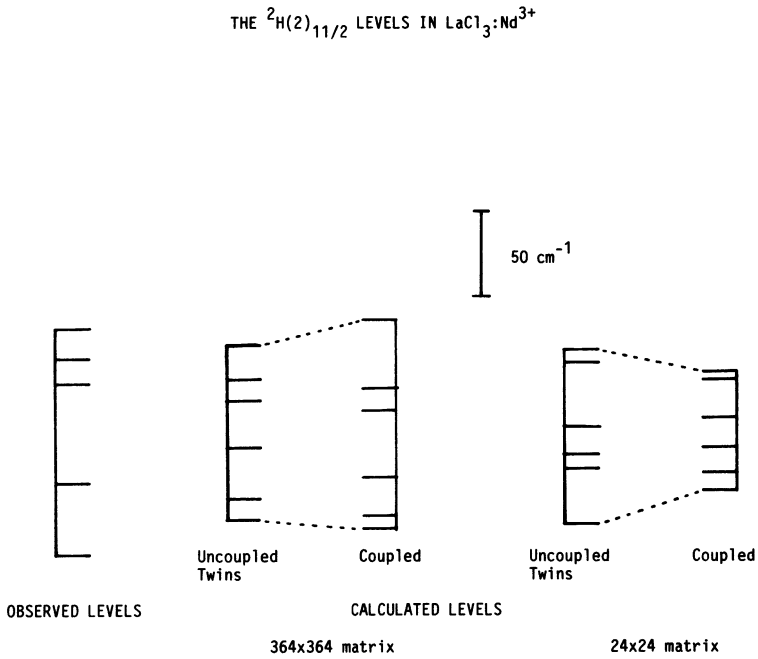
THE $^2H(2)_{11/2}$ LEVELS IN $LaCl_3:Nd^{3+}$
50 cm^{-1}
Uncoupled Twins
Coupled
Uncoupled Twins
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.1.

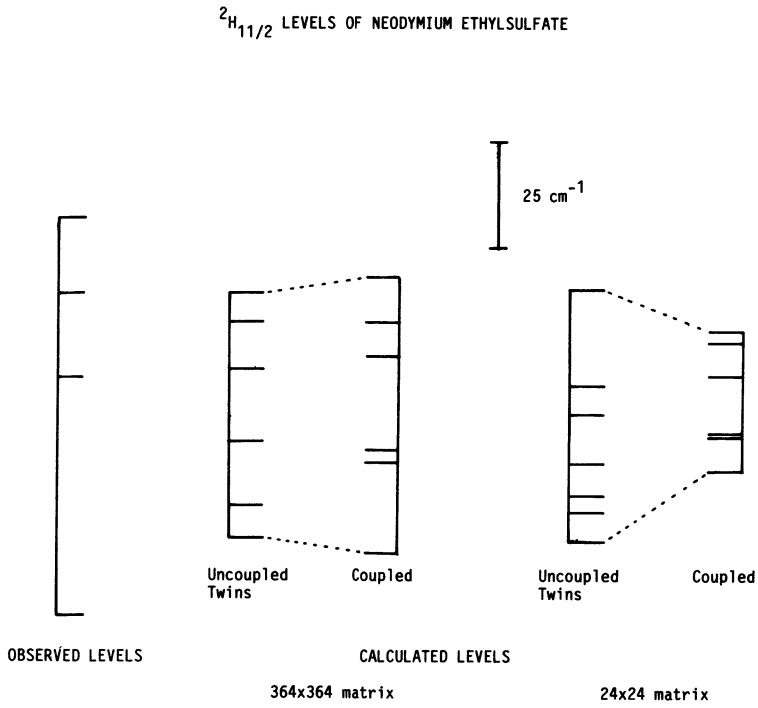
$^2H_{11/2}$ LEVELS OF NEODYMIUM ETHYLSULFATE
25 cm^{-1}
Uncoupled Twins
Coupled
Uncoupled Twins
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.2.

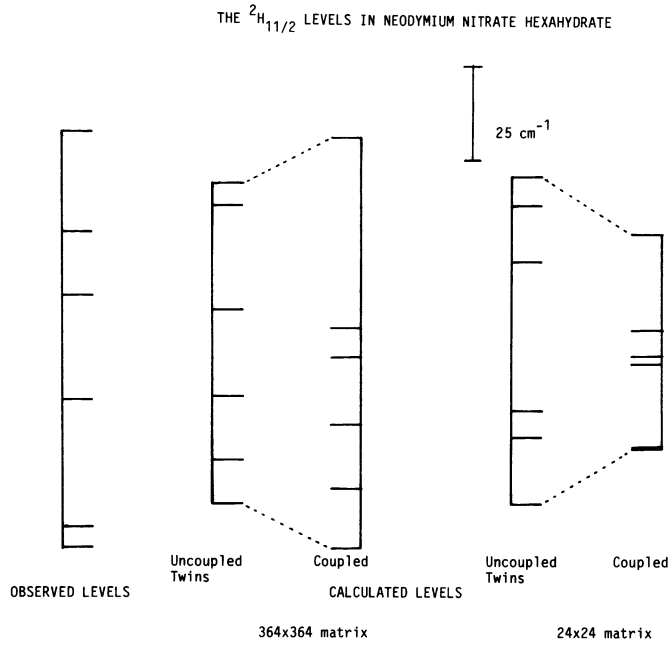
THE $^2H_{11/2}$ LEVELS IN NEODYMIUM NITRATE HEXAHYDRATE
25 cm^{-1}
Uncoupled Twins
Coupled
Uncoupled Twins
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.3.

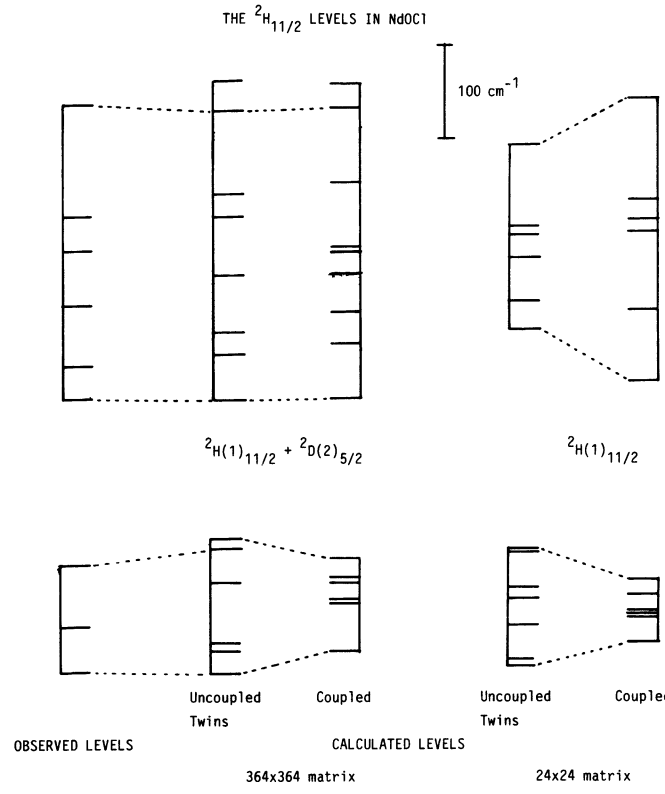
THE $^2H_{11/2}$ LEVELS IN NdOCl
100 cm^{-1}
$^2H(1)_{11/2} + {}^2D(2)_{5/2}$
$^2H(1)_{11/2}$
Uncoupled Twins
Coupled
Uncoupled Twins
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.4.

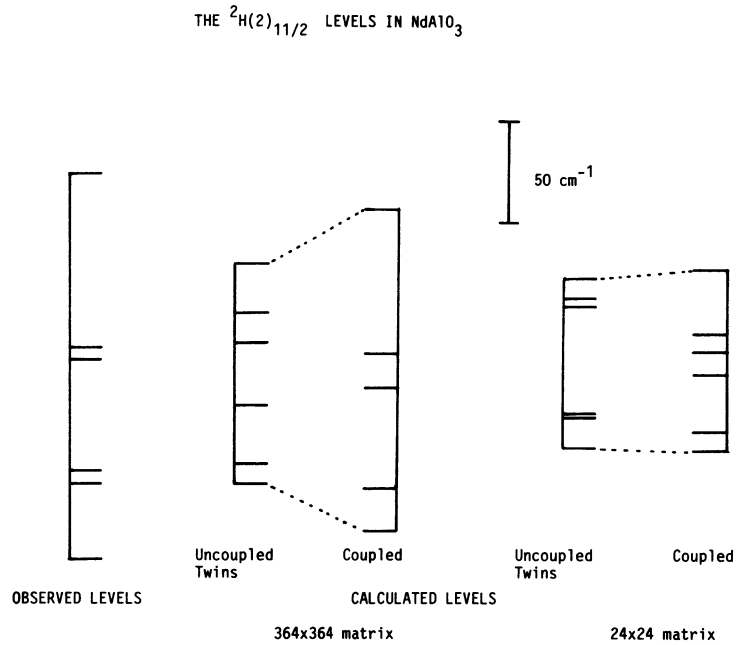
THE $^2H(2)_{11/2}$ LEVELS IN $NdAlO_3$
50 cm^{-1}
Uncoupled Twins
Coupled
Uncoupled Twins
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.5.

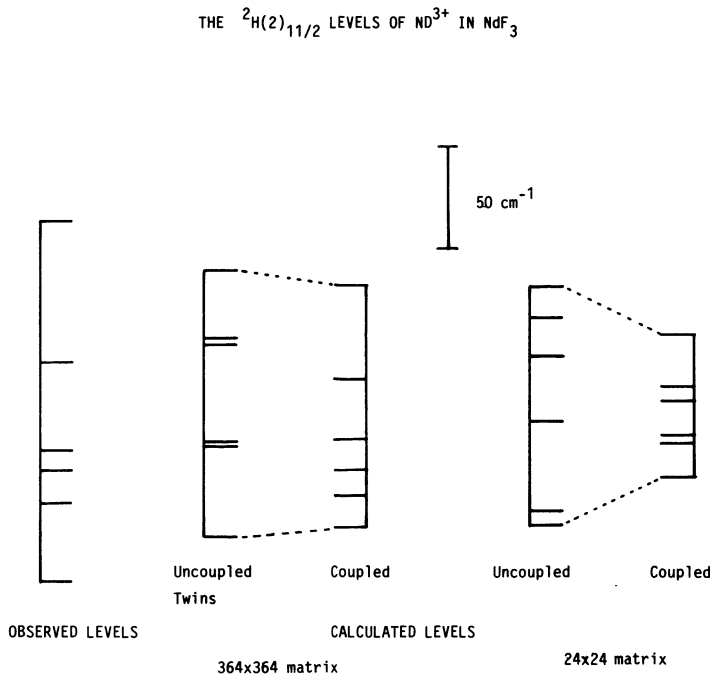
THE $^2H(2)_{11/2}$ LEVELS OF ND^{3+} IN NdF_3
50 cm^{-1}
Uncoupled Twins
Coupled
Uncoupled
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.6.

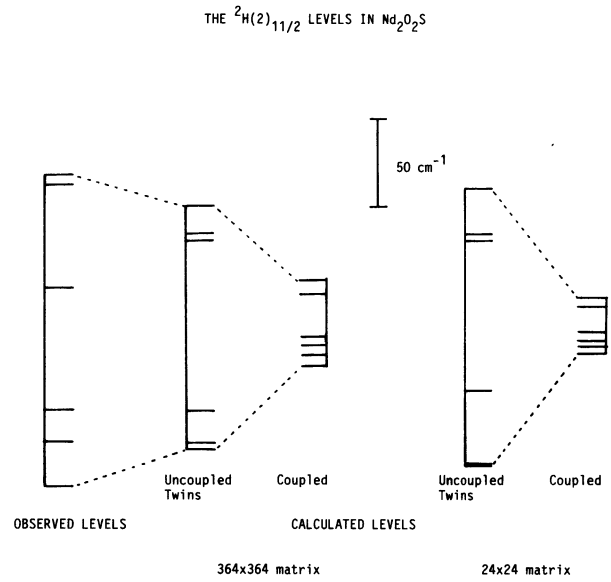
THE $^2H(2)_{11/2}$ LEVELS IN Nd_2O_2S
50 cm^{-1}
Uncoupled Twins
Coupled
Uncoupled Twins
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.7.

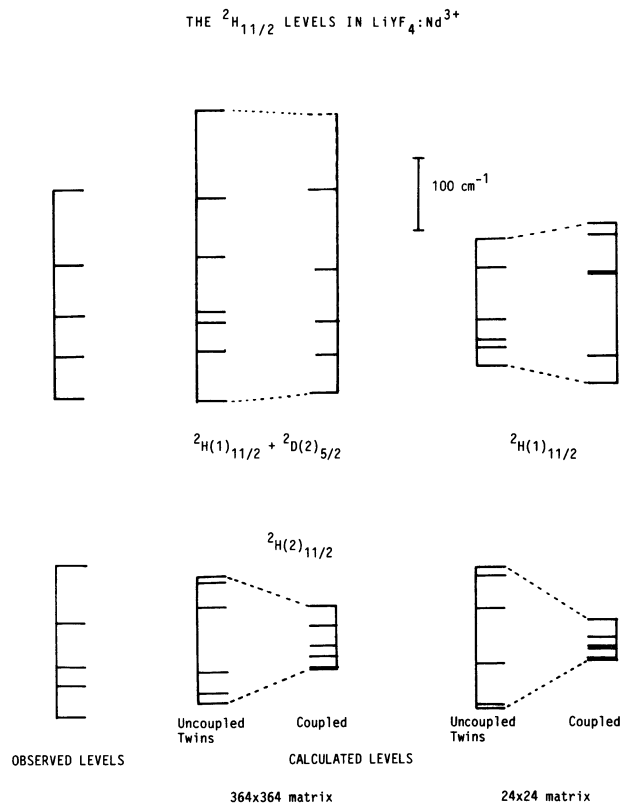
THE $^2H_{11/2}$ LEVELS IN $LiYF_4:Nd^{3+}$
100 cm^{-1}
$^2H(1)_{11/2} + {}^2D(2)_{5/2}$
$^2H(1)_{11/2}$
$^2H(2)_{11/2}$
Uncoupled Twins
Coupled
Uncoupled Twins
Coupled
OBSERVED LEVELS
CALCULATED LEVELS
364x364 matrix
24x24 matrix

Fig. 3.8.

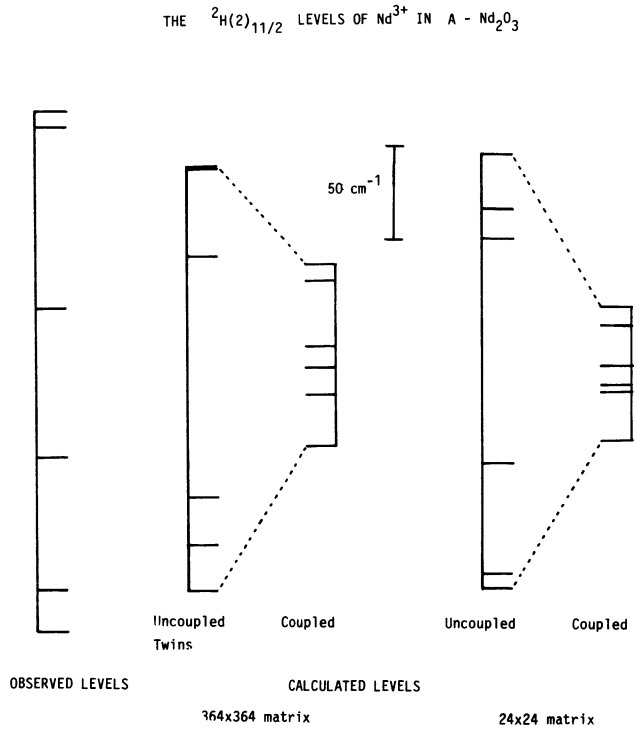

Fig. 3.9.

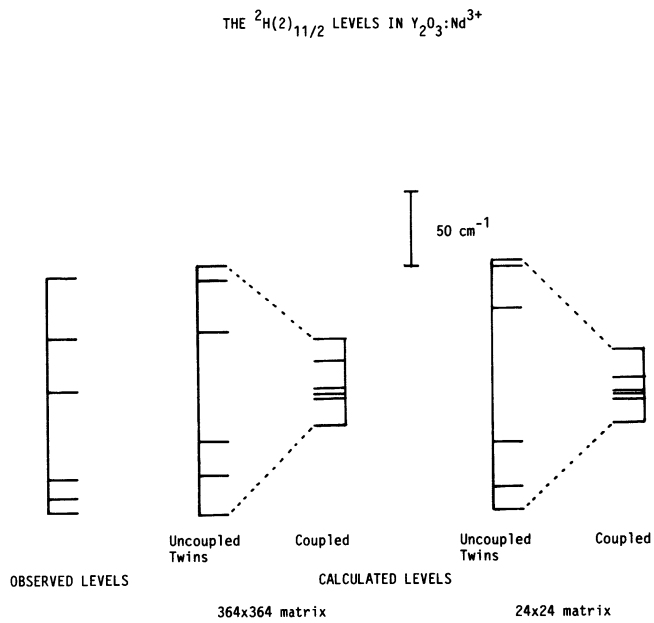

Fig. 3.10.

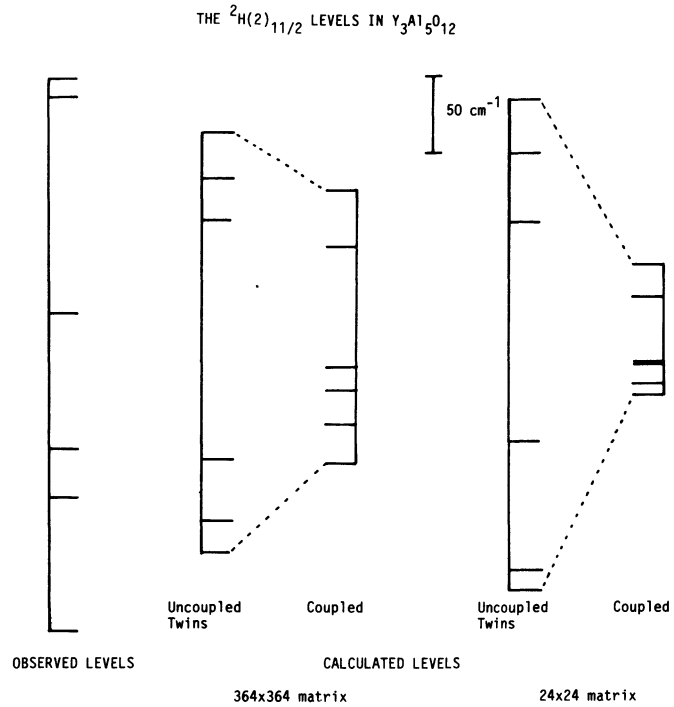

Fig. 3. — (11) The observed and calculated decomposition of the $^2H(2)_{11/2}$ levels in :

1 : $LaCl_3 : Nd^{3+}$
2 : $Nd(C_2H_5SO_4) . 9 H_2O$
3 : $Nd(NO_3)_3 . 6 H_2O$
4 : NdOCl
5 : $NdAlO_3$
6 : NdF_3
7 : Nd_2O_2S
8 : $LiYF_4 : Nd^{3+}$
9 : Nd_2O_3
10 : $Y_2O_3 : Nd^{3+}$
11 : $Y_3Al_5O_{12} : Nd^{3+}$

Table I. — *Correlation between the ratio observed/calculated splitting and the ratio between the uncoupled and coupled splitting.*

Compound	ΔE_o	ΔE_c	$\Delta E_o/\Delta E_c$	ΔE_i	ΔE_{co}	$\Delta E_i/\Delta E_{co}$
$LaCl_3 : Nd^{3+}$	≥ 54	50	≥ 1.08	41	28	1.46
$Nd(C_2H_5SO_4)_3 . 9 H_2O$	≥ 104	64	≥ 1.63	60	33	1.82
$Nd(NO_3)_3 . 6 H_2O$	112	110	1.02	88	58	1.52
NdOCl	≥ 115	78	≥ 1.47	126	68	1.85
$NdAlO_3$	189	156	1.21	83	87	0.50
NdF_3	176	119	1.48	117	71	1.50
Nd_2O_2S	178	42	4.23	156	31	5.03
$LiYF_4 : Nd^{3+}$	217	91	2.38	200	55	3.30
Nd_2O_3	280	97	2.89	234	72	3.25
$Y_2O_3 : Nd^{3+}$	324	160	2.02	333	99	3.36
$Y_3Al_5O_{12} : Nd^{3+}$	360	171	2.11	338	109	3.10

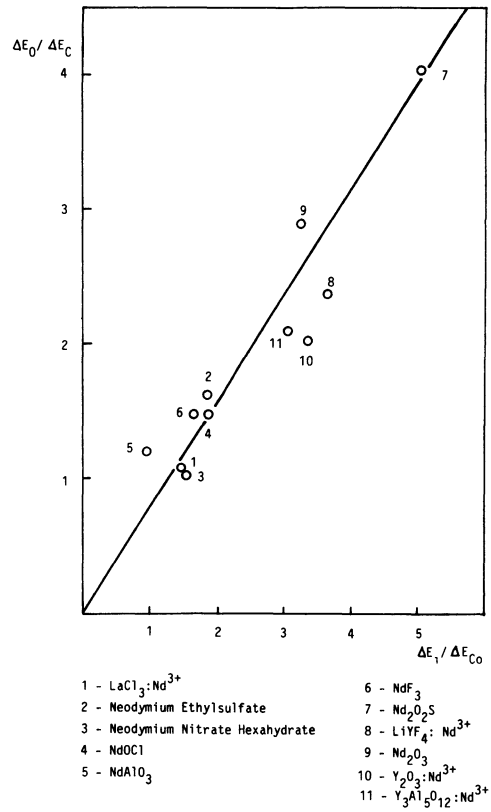

Fig. 4. — Correlation between the relative discrepancy : observed splitting of $^2H(2)_{11/2}$ levels/calculated splitting and the relative contraction due to the coupling between twin ^2H levels.

we choose three B_0^k ($k = 2$, 4 and 6) parameters having the same crystal field strength, i.e. $B_0^2 = 1\,500$, $B_0^4 = 2\,437$ and $B_0^6 = 2\,587\ \mathrm{cm}^{-1}$. Six diagonalizations of the 24×24 matrix are subsequently performed and the resulting splittings are represented figure 5. The coupling results in a drastic reduction of the « splitting efficiency » of B_0^4 and in a mild increase of the efficiency of both B_0^2 and B_0^6. Consequently, we guess that the ratio : observed splitting/calculated splitting more or less behaves like the ratio $R = \bar{E}^4 / (\bar{E}^2 + \bar{E}^6)$ which is reported in table II for the eleven investigated compounds. Indeed, in figure 6 which represents $\Delta E_0/\Delta E_c$ as a function of R, the compounds are rather grouped along a line soaring up for high R values, and curving down to 1 for low R values. The compounds are clustered in the same way in figures 4 and 6. Compounds 1, 3 and 5 form a group with R lower than 0.45, then 2,4 and 6 have an R value lower than 0.69. For 8, 9, 10 and 11, R equals 1.3-1.4, at last compound 7 (oxysulfide) stands alone with $R = 2.02$.

3. Alternative behaviour.

If our assertion is true for $^2H_{11/2}$, in neodymium compounds, it seems as if it should also stand for the $^2H_{11/2}$ levels in Er^{3+} compounds (the complementary configuration of Nd^{3+}). However these levels are correctly fitted in $LiYF_4$ when the calculation is performed within

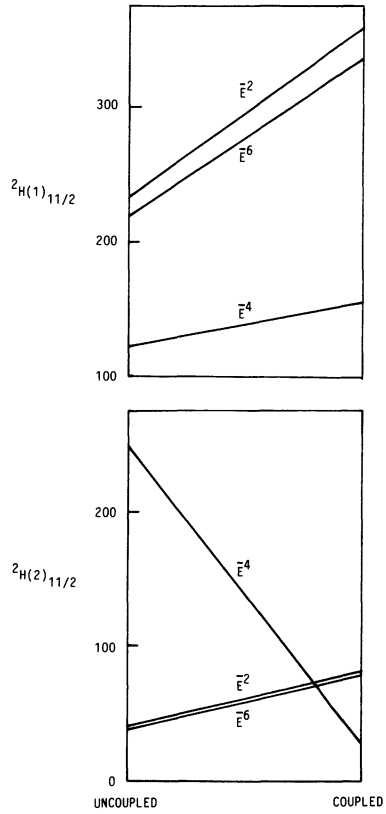

Fig. 5. — Splitting of the $^2H(2)_{11/2}$ levels produced by crystal field parameters of equal strength, for coupled and uncoupled levels.

Table II. — *Crystal Field mean Strength for the second, fourth and sixth order parameters and correlation between the ratio uncoupled/coupled splitting and the* $R = \bar{E}^4/(\bar{E}^2 + \bar{E}^6)$.

Compound	$\bar{E}^2$	$\bar{E}^4$	$\bar{E}^6$	$\bar{E}^4/(\bar{E}^2 + \bar{E}^6)$	$\Delta E_o/\Delta E_c$
$LaCl_3 : Nd^{3+}$	41	52	142	0.35	$\geqslant 1.08$
$Nd(C_2H_5SO_4)_3 \cdot 9\ H_2O$	27	78	150	0.51	$\geqslant 1.63$
$Nd(NO_3)_3 \cdot 6\ H_2O$	69	112	242	0.45	1.02
NdOCl	212	171	131	0.69	$\geqslant 1.47$
$NdAlO_3$	111	104	355	0.28	1.21
NdF_3	75	154	277	0.54	1.48
Nd_2O_2S	45	226	101	2.04	4.23
$LiYF_4 : Nd^{3+}$	96	278	198	1.26	2.38
Nd_2O_3	193	335	168	1.31	2.89
$Y_2O_3 : Nd^{3+}$	273	490	188	1.48	2.02
$Y_3Al_5O_{12} : Nd^{3+}$	126	449	341	1.24	2.11

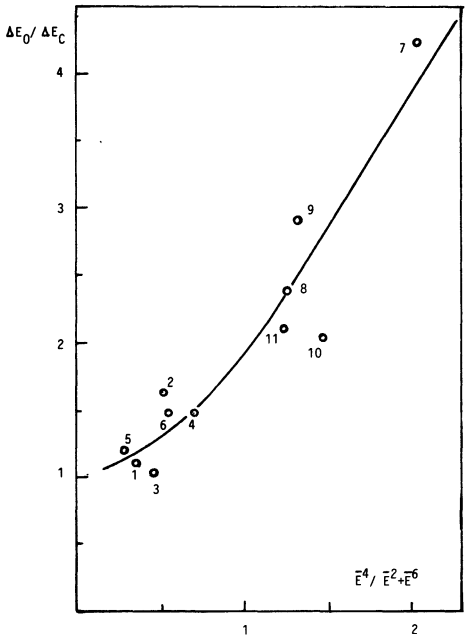

Fig. 6. — Relative discrepancy observed/experimental splitting of the $^2H(2)_{11/2}$ levels as a function of the relative crystal field strength $\bar{E}^4/\bar{E}^2 + \bar{E}^6$. The numbers on the curve refer to the same compounds as in figure 4.

the complete interaction matrix. A mixing between the twin levels, should result in a drastic shrinkage but practically, the mechanism is hindered by a strong mixing with « foreign » levels mainly $^4G_{11/2}$ *via* spin-orbit coupling. The proportion of ^2H in the wavefunctions is only 50 % on the average, whereas it is as high as 90 % in the case of Nd^{3+}. The spin-orbit coupling constant is three times stronger for Er^{3+} than for Nd^{3+}.

4. Fitting absorption spectra.

The hypothesis was made that all the crystal field interactions between « twin » terms with similar S and L in the configuration had to be switched off. This eventual extra selection rule for the crystal field matrix elements can be written as :

$$\langle w, u, S, L, J, M_J | B_q^k . C_q^k | w', u', S, L, J', M_J' \rangle = \delta(w, w') . \delta(u, u') \times \\ \times \langle S, L, J, M_J | B_q^k . C_q^k | S, L, J', M_J' \rangle .$$

The presented scheme corresponds to the introduction of an additionnal delta operator on the crystal field for levels with the same S, L, and J values.

Three Nd^{3+} spectra were chosen in order to perform energy level adjustments with various coupling conditions : the parametric fit of the energy lines of the spectrum was performed by the means of the programs Reel (for real parameters) and Image (for complex parameters) written by one of us [17].

a) $LiYF_4 : Nd^{3+}$: 129 energy levels [11] have been measured up to 40 000 cm^{-1}. The lines of the absorption spectrum are sharp and well-defined. Only five of the six $^2H_{11/2}$ levels have been detected.

b) NdOCl [9] was also experimentally investigated up to 40 000 cm^{-1}. 109 energy levels can be utilized. The position of only three of the $^2H_{11/2}$ lines are known but the corresponding g_z values of these lines have been experimentally measured which should help the assignement.

c) $Y_2O_3 : Nd^{3+}$: the $^2H_{11/2}$ levels are unambiguously measured. Reference [1] reports 85 observed energy levels up to 28 351 cm^{-1}. Unfortunately, the upper $^2H(1)_{11/2}$ levels have not been observed.

4.1 $LiYF_4 : Nd^{3+}$. — A previous work on crystalline $LiYF_4 : Nd^{3+}$ [11, 16] reports the result of a spectroscopic investigation of the compound followed by a parametric interpretations of the energy levels.

129 lines are observed in the absorption spectrum of polycrystalline $LiYF_4 : Nd^{3+}$ recorded at 4 K, over a total of 182 Kramer states in the f^3 configuration.

14 free ion parameters are varied i.e. the electrostatic E^0, E^1, E^2, E^3 Racah parameters, α, β, and γ Trees parameters, T^2, T^3, T^4, T^6, T^7, and T^8 Judd parameters and the spin-orbit coupling parameter ζ. The five crystal field parameters are B_0^2, B_0^4, B_4^4, B_0^6 and B_4^6. The fourteen free-ion parameters mainly fit the barycenters, while the five crystal field parameters are meant to describe the more dainty details of the spectrum.

The hamiltonian is diagonalized on the complete 364×364 basis of the f^3 configuration. The refinement performed by the means of Reel results in the set of parameters listed in table IIIa. The mean deviation is equal to 19.1 cm^{-1} without the $^2H_{11/2}$ levels, to 21.2 cm^{-1} including these levels. The experimental splitting of the $^2H_{11/2}$ level equals 217 cm^{-1}, while the calculated one amounts to 92 cm^{-1} only.

Taking into account the above observations, a second refinement was performed with the crystal field interaction between twin terms switched off. That means that zero values are ascribed to U^2, U^4, and U^6 matrix elements between $^2D(1)$ and $^2D(2)$, $^2F(1)$ and $^2F(2)$, $^2G(1)$ and $^2G(2)$, at last between $^2H(1)$ and $^2H(2)$. The starting crystal field parameters for this new refinement are the previously determined values. After a few cycles, the mean deviation for the 129 levels falls to 16.7 cm^{-1}.

Not only do the calculated $^2H_{11/2}$ levels, but also the others agree better with experimental values. The overall calculated splitting of the $^2H_{11/2}$ level is now equal to 180 cm^{-1} that is, twice the one calculated with coupled levels. As we guessed hereabove, the suppression of the crystal field interaction between twin terms also increases the calculated splitting of the $^2H_{9/2}$ level from 256 to 334 cm^{-1} but does not worsen the parametric adjustment if the assignement of two sub-levels ($^4F_{5/2}$ and $^2H_{9/2}$) is inverted. The newly adjusted crystal field parameters are not very different from the starting set. In table IIIb are listed the experimental and calculated energy levels.

4.2 NdOCl. — The optical absorption of NdOCl was performed on a plate-shaped single crystal [9]. 109 lines have been reported, but only three of them belonging to the lower $^2H_{11/2}$ set. However the values of the magnetic splitting factor g_z of these levels have been measured [18]. The symmetry of the compound is C_{4v}. The parameters to be varied in Reel are the same as above. A first refinement was performed with coupled twins and including the three observed $^2H(2)_{11/2}$ levels. The mean deviation is equal to 18 cm^{-1} for the 109 levels but the assignement of the three experimental $^2H_{11/2}$ levels is questionable since the calculated g_z values disagree with the experimental values. The refinement is not improved by uncoupling U^2, U^4 and U^6 between twins, whereas it is by uncoupling U^4 alone. Then the mean deviation falls to 16.7 cm^{-1} and the g_z values calculated by routine Reel agree better with experimental values in particular for the sub-levels of $^2H_{11/2}$.

Table IIIa. — *Refinement of Crystal Field Parameters of* $LiYF_4 : Nd^{3+}$ *with the crystal field interaction* (CFI) *between twin terms switched off or on.*

Parameter	Value (cm^{-1}) CFI switched off			CFI switched on		
E^0	12 203.9	±	1.0	12 162.6	±	1.0
E^1	4 827.4	±	0.5	4 823.8	±	0.5
E^2	23.65	±	0.01	23.66	±	0.01
E^3	487.4	±	0.1	487.0	±	0.1
α	21.11	±	0.03	20.90	±	0.03
β	– 577.7	±	0.8	– 572.7	±	0.9
γ	1 492.8	±	0.7	1 524.5	±	0.7
T^2	325.6	±	2.3	331.1	±	2.5
T^3	50.6	±	2.1	52.7	±	2.2
T^4	82.4	±	2.3	78.9	±	2.6
T^6	– 289.3	±	4.9	– 282.8	±	5.3
T^7	339.7	±	5.3	325.1	±	6.0
T^8	295.8	±	5.7	302.9	±	5.9
ζ	873.0	±	0.5	873.1	±	0.6
B_0^2	415.6	±	9.2	423.2	±	11.4
B_0^4	– 968.0	±	27.1	– 969.3	±	30.0
B_4^4	– 1 213.7	±	14.8	– 1 204.5	±	16.0
B_0^6	– 66.2	±	27.0	– 5.8	±	27.8
B_4^6	– 1 038.9	±	16.2	– 1 039.43	±	17.1
Mean deviation :						
129 Stark levels	16.7			21.2		
124	(without the $^2H_{11/2}$ set)			19.1		

Table IIIb. — *Experimental and Calculated Energy levels. The twinned levels are typed in bold characters.*

	Exper.	CFI switched off Calc.	Exp.-Calc.	CFI switched on Calc.	Exp.-Calc.
	0	13	– 12	15	– 14
	132	150	– 18	154	– 22
$^4I_{9/2}$	195	210	– 15	203	– 8
	249	261	– 12	256	– 7
	523	539	– 16	545	– 22
	1998	1991	7	1992	6
	2042	2037	5	2030	12
	2042	2032	10	2035	7
$^4I_{11/2}$	2079	2072	7	2070	9
	2228	2229	– 1	2230	– 2
	2264	2263	1	2266	– 2

Table IIIb *(continued)*.

	3948	3936	11	3939	9
	3976	3963	12	3964	12
	3995	3985	10	3983	12
$^4I_{13/2}$	4026	4015	10	4013	13
	4202	4203	– 1	4202	0
	4228	4231	– 4	4232	– 4
	4238	4238	0	4241	– 3
	5851	5850	1	5856	– 5
	5911	5904	7	5908	3
	5947	5955	– 8	5947	0
$^4I_{15/2}$	6026	6026	0	6022	4
	6315	6309	6	6315	0
	6348	6353	– 5	6357	– 9
	6388	6385	3	6377	11
	6432	6420	12	6422	10
$^4F_{3/2}$	11541	11528	13	11523	18
	11598	11575	23	11570	28
	12528	12525	3	12519	9
$^4F_{5/2}$	12558	12566	– 8	12561	– 3
	12677	12666	11	12635-12659	– 24
	12635	**12607**	**28**	**12677-12681**	**– 4**
	12742	**12762**	**– 20**	**12727**	**15**
$^2H(2)_{9/2}$	**12817**	**12822**	**– 5**	**12851**	**– 34**
	12857	**12835**	**22**	**12836**	**21**
	12933	**12941**	**– 8**	**12927**	**6**
	13504	13510	– 6	13506	– 2
	13532	13535	– 3	13526	6
$^4F_{7/2}$	13642	13654	– 12	13652	– 9
	13652	13653	– 1	13651	1
$^4S_{3/2}$	13659	13673	– 14	13674	– 15
	13675	13671	4	13677	– 2
	14769	14784	– 15	14766	3
	14795	14807	– 12	14790	5
$^4F_{9/2}$	14814	14877	– 63	14884	– 70
	14894	14888	6	14897	– 3
	14966	14932	34	14953	13
	15941	**15964**	**– 23**	**16020**	**– 79**
	15987	**15978**	**9**	**16040**	**– 53**
$^2H(2)_{11/2}$	**16013**	**16012**	**1**	**16053**	**– 40**
	16077	**16099**	**– 22**	**16078**	**– 1**
	16158	**16145**	**13**	**16110**	**48**
	17182	17182	0	17185	– 3
	17292	17267	25	17265	27

Table IIIb *(continued)*.

$^4G_{5/2}$	17322	17323	– 1	17325	– 3
	17431	17443	– 12	17413	18
$^4G_{7/2}$	17443	17433	10	17422	21
	17498	17462	36	17493	5
$^2G_{7/2}$	17674	17652	22	17659	15
	19055	19070	– 15	19041	14
	19102	19091	11	19085	17
	19172	19187	– 15	19194	– 22
	19201	19193	8	19212	– 11
	19569	19580	– 11	19575	– 6
	19627	19614	13	19627	0
$^4G_{9/2}$	19685	19706	– 21	19706	– 21
	19732	19724	8	19727	5
$^2K_{13/2}$	19771	19766	5	19770	1
	19833	19818	15	19812	21
	19990	20010	– 20	20012	– 22
	20040	20023	17	20028	12
	21066	**21050**	**16**	**21036**	**30**
	21079	**21076**	**3**	**21078**	**0**
$^2G(1)_{9/2}$	**21084**	**21091**	**– 7**	**21107**	**– 23**
	21119	**21100**	**19**	**21112**	**7**
	21295	**21319**	**– 24**	**21327**	**– 32**
$^2D(1)_{3/2}$	**21358**	**21352**	**6**	**21348**	**10**
	21459	21468	– 9	21467	– 8
	21565	21592	– 27	21589	– 24
$^4G_{11/2}$	21729	21755	– 26	21758	– 29
	21768	21779	– 11	21783	– 15
$^2K_{15/2}$	21834	21832	2	21829	5
	21858	21843	15	21842	16
	21920	21937	– 17	21925	– 5
	21968	21978	– 10	21970	– 2
	22012	22021	– 9	22015	– 4
$^2P_{1/2}$	23420	23421	– 1	23423	– 3
	23923	**23929**	**– 6**	**23923**	**0**
$^2D(1)_{5/2}$	**23952**	**23962**	**– 10**	**23963**	**– 11**
	24056	**24038**	**18**	**24040**	**16**
	26295	26285	10	26297	– 2
$^2P_{3/2}$	26385	26358	27	26358	27
	28137	28111	26	28118	19
$^4D_{3/2}$	28249	28244	5	28244	5
	28409	28403	6	28404	5
$^4D_{5/2}$	28563	28570	– 7	28567	– 4
	28612	28609	3	28606	6
$^4D_{1/2}$	28835	28869	– 34	28867	– 32
	29240	29264	– 24	29248	– 8

Table IIIb *(continued)*.

$^2I_{11/2}$	29326	29336	− 10	29323	3
	29412	29417	− 5	29412	0
	29771	29712	59	29722	49
	30248	30251	− 3	30250	− 2
$^2L_{15/2}$	30395	30390	5	30394	1
	30590	30588	2	30586	4
$^4D_{7/2}$	30684	30668	14	30674	10
	30769	30761	8	30759	10
$^2I_{13/2}$	30921	30922	− 1	30919	2
	31066	31076	− 10	31072	− 6
	31807	31774	33	31773	34
	31827	31830	− 3	31829	− 2
$^2L_{17/2}$	31878	31901	− 23	31906	− 28
	31959	31935	24	31942	17
	32113	32133	− 20	32139	− 26
$^2H(1)_{9/2}$	**33014**	**33037**	**− 23**	**33028**	**− 14**
	33124	**33136**	**− 12**	**33143**	**− 19**
$^2D(2)_{3/2}$	**33456**	**33459**	**− 3**	**33483**	**− 27**
	33546	**33570**	**− 24**	**33570**	**− 24**
	34258	**34250**	**8**	**34256**	**2**
	34317	**34317**	**0**	**34324**	**− 7**
$^2H(1)_{11/2}$	**34376**	**34377**	**− 1**	**34351**	**25**
	34447	**34455**	**− 8**	**34441**	**6**
	34554	**34537**	**17**	**34536**	**18**
	38491	**38522**	**− 31**	**38578**	**− 87**
$^2F(2)_{5/2}$	**38700**	**38707**	**− 7**	**38677**	**23**
	38789	**38789**	**0**	**38753**	**36**
	39936	**39913**	**23**	**39981**	**− 45**
$^2F(2)_{7/2}$	**40096**	**40115**	**− 19**	**40065**	**31**
	40193	**40160**	**33**	**40159**	**34**

The calculated and experimental g_z values are listed in table IV, compared with previously determined values. The sets of crystal field parameters determined with coupled and uncoupled twins are listed in table V. As occurs for $LiYF_4 : Nd^{3+}$ the two sets are quite similar.

4.3 $Y_2O_3 : Nd^{3+}$. — 85 experimental levels over 111 have been observed up to 28 369 cm^{-1} [1, 12]. The position of the higher $^2H(1)_{11/2}$ levels (at about 33 000 cm^{-1}) have not been reported. The refinement was carried out with Image on completely uncoupled twins. The lowest mean deviation (20.4 cm^{-1}) is obtained for the set of parameters listed in table VI. If the $^2H_{11/2}$ are discarded, the deviation is slightly lower : 19.3 cm^{-1}. When the twin level is coupled, the lowest deviation is equal to 17.4 cm^{-1} without the $^2H_{11/2}$ levels and 24.7 cm^{-1} when they are included in the refined set.

Table IV. — *Magnetic Splitting Factors for Stark levels in* NdOCl.

Energy (cm^{-1})	Nominal State	Ref. [18]	Coupled Ref. [18]	Uncoupled
13180	^{4}F7/2-7/2	9.17	8.35	8.35
14497	^{4}F9/2 9/2	7.90	10.26	10.62
14520	^{4}F9/2-7/2	3.35	7.38	7.76
14573	^{4}F9/2-5/2	4.84	3.84	3.95
14689	^{4}F9/2 3/2	1.31	1.20	1.38
14711	^{4}F9/2 1/2	1.14	0.72	0.77
15772	^{2}H(2)11/2-11/2	3.46	12.00	4.98
15886	^{2}H11/2 3/2	1.04	3.20	0.64
	^{2}H11/2 9/2		8.03	4.43
16818	^{4}G5/2 1/2	1.23	0.19	0.63
16853	^{4}G5/2-5/2	1.49	0.68	0.31
17061	^{4}G7/2 1/2	0.48	0.53	3.58
18749	^{4}G7/2-7/2	5.27	5.94	5.88
18771	^{4}G7/2-5/2	3.78	4.35	4.39
18806	^{4}G7/2 1/2	1.41	0.26	0.22
18871	^{4}G7/2 3/2	0.79	2.11	2.13
19171	^{4}G9/2 1/2	3.18	2.99	2.10
19192	^{4}G9/2 1/2	3.81	2.97	1.78
19271	^{4}G9/2-7/2	7.8	7.73	7.87
19309	^{4}G9/2-5/2	4.12	4.03	3.88
19789	^{2}K13/2 13/2	11.3	12.09	11.98
20771	^{2}G(1)9/2 9/2	11.76	9.97	9.84
20780	^{2}G(1)9/2-7/2	7.96	8.05	8.00
20993	^{2}K15/2	1.38	0.11	0.13
21046	^{4}G11/2 3/2	0.75	2.34	1.98
21775	^{2}K15/2 15/2	12.39	15.6	15.60
22971	^{2}P1/2 1/2	0.87	0.68	0.68
23399	^{2}D(1)5/2-5/2	6.42	5.95	5.98
23687	^{2}D(1)5/2 1/2	2.42	1.23	1.22

5. Search for a crystal field operator.

The results obtained in the preceding paragraph are rather satisfactory and seem to correspond to a kind of selection rule related to the labels of the higher order R_7 and G_2 groups associated with the free ion levels. There is no obvious reason for such a formal selection rule. It is clear however that its application produces an uncoupling of the levels wich suppresses the constriction illustrated in figure 2, and generally improves the fitting of calculated to observed levels within the configuration.

It is worth mentionning that, without uncoupling, the application of an additional crystal field operator to the $^2H(2)_{11/2}$ levels allows also a reasonable agreement with experimental results. This operator has the form of an additional C_0^2 associated with a strong

Table V. — *Crystal Field Parameters of* NdOCl *with the crystal field interaction* U^4 *between twin terms switched off or on.*

Parameter	Value (cm^{-1}) CFI (U^4) switched off			CFI (U^4) switched on		
E^0	11 622.0	±	1.1	11 641.9	±	1.1
E^1	4 689.2	±	0.5	4 692.8	±	0.5
E^2	22.97	±	0.01	22.97	±	0.01
E^3	472.9	±	0.1	473.5	±	0.1
α	19.31	±	0.03	19.48	±	0.03
β	− 612.7	±	0.8	− 618.1	±	0.9
ξ	1 782.8	±	0.7	1 767.54	±	0.7
T^2	388.1	±	2.9	371.2	±	3.0
T^3	33.4	±	2.4	32.4	±	2.5
T^4	75.4	±	2.6	76.1	±	2.7
T^6	− 247.2	±	5.4	− 245.9	±	5.6
T^7	306.1	±	6.5	307.5	±	6.7
T^8	297.1	±	5.5	289.7	±	5.7
ζ	868.97	±	0.59	869.08	±	0.61
B_0^2	− 895.2	±	9.7	− 895.3	±	10.0
B_0^4	− 318.4	±	25.9	− 310.5	±	26.4
B_4^4	− 878.4	±	18.1	− 879.7	±	19.2
B_0^6	865.7	±	24.1	873.0	±	25.1
B_4^6	− 234.0	±	24.8	− 231.6	±	26.8
Mean deviation (cm^{-1}) 109 Stark levels	16.7			18		

B_0^2 parameter (in the 3 000 cm^{-1} range). (Of course, this treatement cannot be applied to the other $^{2sc+1}L_J$ levels). By varying the B_0^2 parameter, the experimental results for $^2H_{11/2}$ can be fitted in a rather good way, sometimes better than with the preceding scheme involving uncoupling (Figs. 7 and 8). This is especially true for Nd_2O_2S (B_0^2 (normal) + B_0^2 (special) = 3 200 cm^{-1}),

$$NdF_3(B_0^2(n) + B_0^2(s) = 1\,600\ cm^{-1}),$$
$$NdAlO_3(B_0^2(n) + B_0^2(s) = 2\,000\ cm^{-1}),$$
$$A\text{-}Nd_2O_3(B_0^2(n) + B_0^2(s) = 4\,000\ cm^{-1}).$$

The crystal field of all these compounds is described with respect to the C_3 axis. As a matter of fact, a quite good fitting is found also for the C_2 site of Nd^{3+} in C-Y_2O_3, but using the c.f.p. for the trigonal S_6 site and a

$$(B_0^2(n) + B_0^2(s) = 4\,400\ cm^{-1}).$$

The fit is acceptable but not as good as in the preceding case for Nd^{3+} in $LiYF_4$ and Nd^{3+} : $Y_3Al_5O_{12}$ which are described with respect to a C_4 axis. The same is true for the C_{4v} site of NdOCl for which experimental data are however uncomplete.

Table VI. — *Crystal Field Parameters of* $Y_2O_3 : Nd^{3+}$ *with the crystal field interaction between twin terms switched off or on.*

Parameter	Value (cm^{-1}) CFI (U^4) switched off			CFI (U^4) switched on		
E^0	12 912.8	±	1.4	12 914.5	±	1.5
E^1	4 841.8	±	1.1	4 848.4	±	1.1
E^2	(22.80)			(22.80)		
E^3	467.9	±	0.1	468.2	±	0.1
α	19.01	±	0.05	19.57	±	0.05
β	− 621.0	±	1.2	− 637.7	±	1.3
γ	(753.00)			(753.00)		
T^2	370.2	±	2.9	370.2	±	2.6
T^3	(44.50)			(44.50)		
T^4	100.4	±	3.1	100.4	±	3.1
T^6	− 295.8	±	7.3	− 295.8	±	6.6
T^7	(120.0)			(120.0)		
T^8	(437.0			(437.0)		
ζ	868.1	±	0.7	868.1	±	0.8
B_0^2	− 428.2	±	30.5	− 402.6	±	34.3
B_2^2	− 848.8	±	14.7	− 881.9	±	15.7
B_0^4	− 1 138.8	±	51.2	− 1 322.9	±	58.4
RB_2^4	− 1 740.7	±	23.2	− 1 644.0	±	26.4
IB_2^4	(0.0)			318.3	±	83.9
RB_4^4	1 046.1	±	33.4	915.5	±	37.3
IB_4^4	− 730.2	±	50.2	− 1 018.3	±	57.2
B_0^6	195.9	±	84.5	250.8	±	92.6
RB_2^6	493.7	±	43.7	630.9	±	45.1
IB_2^6	(0.0)			(0.0)		
RB_4^6	777.4	±	30.7	689.3	±	32.8
IB_4^6	− 569.3	±	35.0	− 623.8	±	41.2
RB_6^6	36.0	±	35.0	− 28.7	±	41.0
IB_6^6	(0.0)			− 55.5	±	42.0
Mean deviation (cm^{-1}) 85 Stark levels	20.5			24.7		

A simple crystal field operator such as C_0^2 has the effect of lifting the degeneracy of the « constricted » coupled level but the associated parameter has to display a high, « unrealistic » value. An analogous result has been obtained by using an « unrealistic » value of the free atom E^2. C_0^2 is much more efficient to yield results looking quite alike experimental data than C_0^4 or C_0^6. The previous analysis has shown that the values of the fourth order c.f.p. are critical in cases where the discrepancies between calculated and observed values are large. The use of an additional C_0^2 appears then as a simple way to correct empirically this effect.

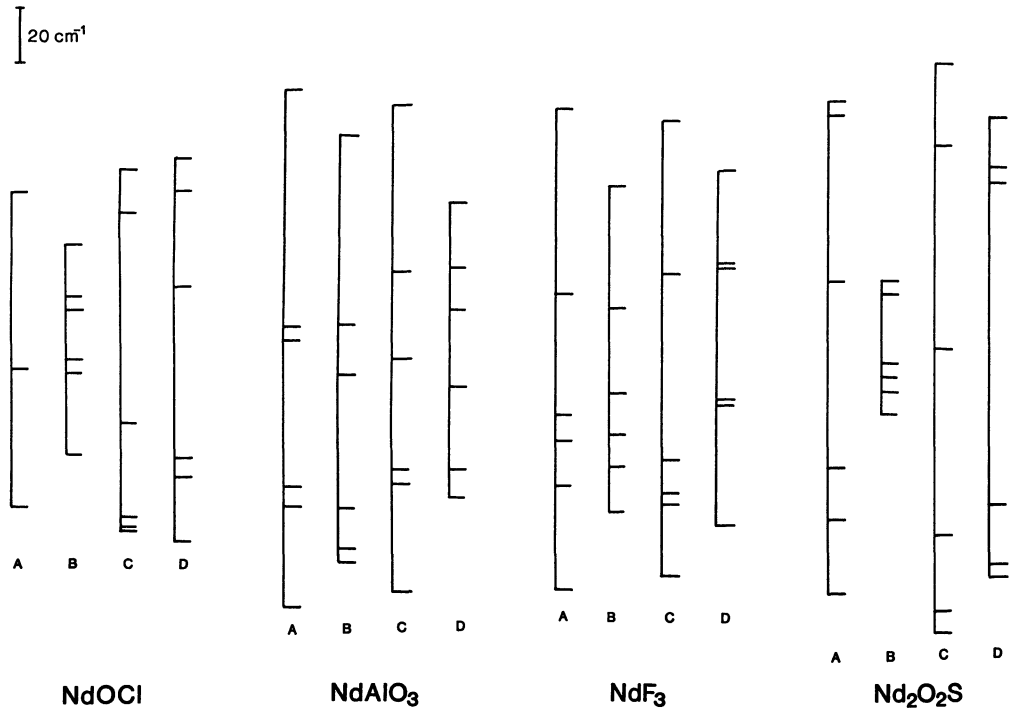

Fig. 7. — The simulation of $^2H(2)_{11/2}$ splittings with a B_0^2 crystal field operator for NdOCl, $NdAlO_3$, NdF_3 and Nd_2O_2S. A corresponds to observed levels, B and C are calculated values with B_0^2 values listed hereafter and D is the splitting represented on the quoted figure.

NdOCl $B_0^2 = -920$ and $2\,400\ cm^{-1}$, figure 3-4.
$NdAlO_3$ $B_0^2 = -481$ and $1\,000\ cm^{-1}$, figure 3-5.
NdF_3 $B_0^2 = 201$ and $1\,600\ cm^{-1}$, figure 3-6.
Nd_2O_2S $B_0^2 = 170$ and $3\,200\ cm^{-1}$, figure 3-7.

6. Conclusion.

The obvious discrepancy between calculated and experimental values in the case of the crystal field splitting of $^2H(2)_{11/2}$ levels is the sign that « something » is missing in the ordinary crystal field theory of the $4f^n$ configurations in solids. It is clear that we are not facing a simple truncation effct in the calculation.

Two other famous discrepancies have been extensively studied. The first one concerns the experimental $^3K_8$ sublevels of Ho^{3+} in $LaCl_3$ [19], 35 % more spreaded than the calculation predicts. This is a small discrepancy compared to those usually displayed by the $^2H(2)_{11/2}$ levels of Nd^{3+}. The extra-splitting in $^3K_8$ can be well reproduced by adding the effects of *Spin Correlated Crystal Field* (SCCF), involving a two-electron parametrization. The SCCF is contained in the general correlation field parametrization of Bishton and Newman [20], was anticipated by Newman [21], considered for this particular case by Judd [22], and fully fitted by Crosswhite and Newman [23]. The operator is meant to account for the dependence of the 4f electron radial wave function on its spin direction with respect to the total spin. The same model was utilized with success to improve the experimental/calculated

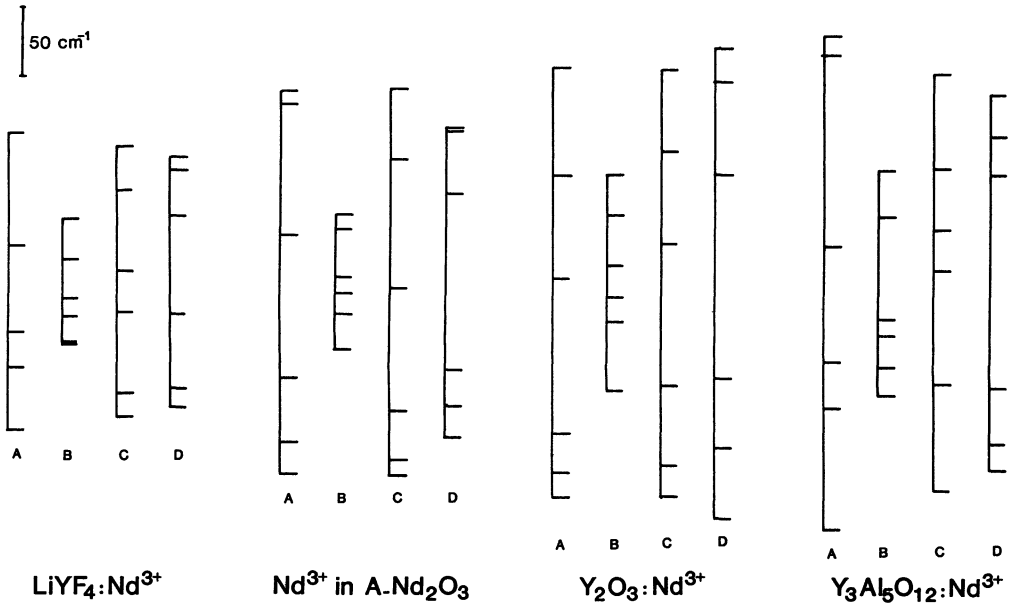

Fig. 8. — Idem for :

$LiYF_4 : Nd^{3+}$ $B_0^2 = 401$ and $3\,000\ cm^{-1}$, figure 3.8.
Nd_2O_3 $B_0^2 = -836$ and $4\,000\ cm^{-1}$, figure 3-9.
$Y_2O_3 : Nd^{3+}$ $B_0^2 = -1\,735$ and $4\,400\ cm^{-1}$, figure 3-10.
$Y_3Al_5O_{12} : Nd^{3+}$ $B_0^2 = 514$ and $3\,000\ cm^{-1}$, figure 3-11.

agreement in the case of the $^3K_8$ level in $Cs_2NaYCl_6 : Ho^{3+}$ by Reid and Richardson [24]. However, in this latter case, the discrepancy experimental/calculated is less pronounced than for $LaCl_3$ (about 10 % for the overall splitting).

Also mis-behaving is the $^1D_2$ level of $4f^2$ (Pr^{3+}) in $LaCl_3$ (or $PrCl_3$). The discrepancy which is of the order of 50 % for the total splitting [25, 26] is also less pronounced than for the $^2H(2)_{11/2}$ levels. Van Siclen [27] examined the eventuality of term dependent crystal field parameters originating from polarisable neighbours. The effect was too small to account for the observed discrepancy.

Then, by analogy with the SCCF, Yeung and Newman suggested [28] an *Orbitally Correlated Crystal Field* which was tested on $LaCl_3 : Pr^{3+}$. A much better agreement was stated within the $^1D_2$ sublevel (rms falling from 17.7 to 12.1 cm^{-1}).

Recently, in a complete configuration interaction calculation involving $4f^2$ and the nearest excited configuration 4f 5d, Garcia and Faucher [29] refined the conventional one-electron crystal field parameters within the complete basis set and obtained a similar agreement for the splittings of the $^1D_2$ levels. It is not really surprising since the LCCF is contained in the full correlation crystal field [20] which in turn reproduces the features of configuration interaction.

In the case of the $^2H(2)_{11/2}$ levels in Nd^{3+}, Souza da Gama [16] had some success by testing the SCCF restricted to the small 24×24 dimensionned $^2H(2)_{11/2}$ matrix in $LiYF_4 : Nd^{3+}$.

However, it seems that, up to now, the models involving two-electron operators have not been able, when applied in the complete $4f^3$ configuration, to produce the enormous

corrections needed to adjust experiment and crystal field model in the case of the $^2H(2)_{11/2}$ levels of Nd^{3+}.

Judd [30] mentions other possible corrections due to charge transfer mechanisms (electron migrating from the ligand to the rare earth shell) giving rise to high rank ($k > 6$) operators, but suspects that the resulting contributions would be weak.

Possibly, the total correlation crystal field could be efficient but the number of coefficients is enormous and all the effects have to converge to yield hage specific effects needed to handle the enormous observed deviations.

The empirical operators described in this work have the advantage of a crude simplicity together with a high specific efficiency. A special E^2 or a special B_0^2 value utilized for the $^2H_{11/2}$ pair, lifts the pseudo-degeneracy of the lower level and leads to a good agreement with experience.

Besides, we stated in the case of 11 compounds, that the $^2H(2)_{11/2}$ level ($4f^3$) is more or less tightly contracted when it is coupled with its twin and this contraction is narrowly connected with the experimental/calculated discrepancy.

The $^2H(2)_{11/2}$ level is all the more affected by the coupling with its twin that it is a « pure twin » level. In the case of its homologue in Er^{3+}, the phenomenon is smeared by a high spin-orbit coupling with other levels.

Therefore, if « something » is missing in crystal field treatment, something connected to the binding between twins, it is not surprising that the $^2H_{11/2}$ levels be specially touched and stand as an unique foreign set among a hundred of otherwise neatly fitted spectral levels.

Possibly, is it not a mere suppression of the coupling which is required but a tuning of U^2, U^4 and U^6 following the compound. Our steps are empirical, but perhaps experimental evidences such as those presented here can help to find a theoretical explanation.

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