

Lawrence Berkeley National Laboratory

Recent Work

Title

CONFIGURATION INTERACTION EFFECTS ON THE "FREE ION" ENERGY LEVELS OF Nd³⁺ AND Er³⁺

Permalink

<https://escholarship.org/uc/item/18n459qd>

Author

Rajnak, K.

Publication Date

1964-12-02

University of California
Ernest O. Lawrence
Radiation Laboratory

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

CONFIGURATION INTERACTION EFFECTS ON THE "FREE ION"
ENERGY LEVELS OF Nd^{3+} AND Er^{3+}

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

CONFIGURATION INTERACTION EFFECTS ON THE "FREE ION"
ENERGY LEVELS OF Nd^{3+} AND Er^{3+}

K. Rajnak

December 2, 1964

CONFIGURATION INTERACTION EFFECTS ON THE "FREE ION"

ENERGY LEVELS OF Nd^{3+} AND Er^{3+} *

K. Rajnak

Lawrence Radiation Laboratory
University of California
Berkeley, California

December 2, 1964

ABSTRACT

Using 3 or 4 parameters of configuration interaction, the experimental "free ion" energy levels of Nd^{3+} and Er^{3+} have been fit with an r.m.s. deviation of $45 - 55 \text{ cm}^{-1}$. The significance of the various parameter values is discussed. It is also shown that assignments based purely on comparison with a calculation using only F_2 , F_4 , F_6 and ζ may occasionally be in error. Several discrepancies in previous work are now cleared up.

* This work was done under the auspices of the U. S. Atomic Energy Commission.

I. INTRODUCTION

Although it has been recognized for some time that the effects of configuration interaction on the energy levels of triply ionized rare earth ions may not be negligible, few attempts have been made to include them explicitly in the calculation of the electrostatic energy levels.^{1,2} Most discussions of configuration interaction in these ions have been concerned with the effects on the crystal field splittings and crystal field parameters³⁻⁶ rather than on the free ion levels. There are, however, also configuration interaction effects characteristic of the free ion which may be more important than those arising from the crystal field. A large portion of these effects are automatically taken into account if the Slater integrals F_2 , F_4 , F_6 and the spin-orbit coupling constant ζ are treated as variable parameters to be determined from the experimental data.⁷ But, there are also overt effects which can be included only by use of the additional parameters α , β and γ which arise from the linear theory of configuration interaction and the "non-linear" parameters $Y(kk', l')$ which result from interactions with configurations differing from f^N in the quantum numbers of only one electron.⁷

A least squares fit of the four Slater parameters usually reproduces the observed "free ion" energy levels with an rms deviation of 50 - 150 cm^{-1} .^{2,5,6,8} An improvement of about 20 cm^{-1} is sometimes obtained when the term $\alpha L(L+1)$ is included.² The total effects of configuration interaction, however, arise from the sum of several terms which may be of different signs and comparable magnitude. Thus the results may be somewhat misleading if only one term is used.

In a recent calculation⁹ (hereafter referred to as I), including both linear and non-linear parameters of configuration interaction, it was possible to fit 37 of the 41 levels of the $4f^3$ configuration of Pr^{2+} with an r.m.s. deviation of $\pm 29 \text{ cm}^{-1}$. It is now of interest to study the variation of the configuration interaction parameters as a function of the degree of ionization and of atomic number by carrying out a similar calculation on triply ionized rare earth ions at both ends of the periodic table. Unfortunately, the only extensive data available on the triply ionized rare earths come from absorption and fluorescence data on various crystals. The "free ion" levels are obtained as the centers of gravity of groups of crystal field levels. In many cases, however, all of the crystal field components of a particular SLJ level are not observed experimentally and their positions must be determined from a crystal field calculation. This introduces an uncertainty in the experimental "free ion" levels which depends on the number of crystal field components observed and the accuracy of the crystal field calculation. Another problem in determining "free ion" energy levels from crystal data is the shift in the centers of gravity of the crystal field levels due to J-mixing by the crystal field. The amount of this shift is a function of the crystal field strength and the energy difference between interacting levels. The recent calculations of Eisenstein^{5,6} in which he diagonalized the electrostatic, spin-orbit and crystal field energy matrices simultaneously for both Nd^{3+} and Er^{3+} in LaCl_3 provide a basis for determining the magnitude of this shift. The differences between the centers of gravity of the crystal field components resulting from this calculation and the SLJ-levels

calculated by diagonalizing the electrostatic and spin-orbit matrices alone for the same values of F_2 , F_4 , F_6 and ζ should give, to a first approximation, the crystal field shift of each SLJ-level. If these crystal field shifts are then subtracted from the corresponding experimental centers of gravity, a set of "free ion" energy levels is obtained. These are then the appropriate levels to be fit in a least squares calculation of the relevant electrostatic parameters. The "free ion" levels given in Table I for Nd^{3+} and Table IV for Er^{3+} in LaCl_3 were derived in this manner.

The fitting procedure is identical to that discussed in I. As before, the r.m.s. deviation σ is defined as

$$\sigma = \sqrt{\frac{\sum_i \Delta_i^2}{N-K}}$$

where Δ_i is the deviation of the i^{th} level, N is the number of levels fit and K is the number of parameters. This definition of σ allows comparison of calculations involving different numbers of free parameters. In all cases E^0 , which affects the center of gravity of the configuration but not the splitting, has been included as a parameter in the determination of K .

The choice of the "non-linear" configuration interaction parameters and their physical significance has also been discussed previously in considerable detail.⁹ These results are only summarized here and the reader is referred to I for further details. The parameters α , β , and γ are the coefficients of $L(L+1)$, $G(G_2)$, and $G(R_7)$ respectively. They arise mainly from interactions with configurations differing from f^N in the quantum numbers of two electrons, but also contain some contributions from one-electron substitutions. α is expected to be positive; β , negative. γ affects only the position of the $(100) (10)^2 F$

term relative to the other terms. Since no 2F levels have been observed in either Nd^{3+} or Er^{3+} crystals, this parameter is not applicable in the present calculations. The parameters $Y(kk', l')$ result from interaction with configurations differing from f^N in the quantum numbers of only one electron. The most important terms are expected to be those where $l' = 1$ and 3 , i.e. where the substituted electron is in a p or an f state. $Y(kk', l')$ involves the radial integrals $R^k(4f; 4f; 4f n' l')$ and $R^{k'}(4f; 4f; 4f n' l')$ and is expected to be largest for smaller values of k and k' . $Y(kk', l')$ will be positive if the interaction is between $4f^N$ and $n' l' 4l'+1$ $4f^{N+1}$ and negative if it is between $4f^N$ and $4f^{N-1} n' l'$. Thus $Y(kk', 1)$ may have either sign depending on which interaction is dominant. $Y(kk', 3)$ must be negative for rare earths since there is no filled f shell from which to excite an electron.

II. RESULTS

The calculations have been carried out for Nd^{3+} in LaCl_3 and for three different crystals containing Er^{3+} . In all cases the r.m.s. deviation is improved from 100 - 150 cm^{-1} to 80 - 85 cm^{-1} when the parameters α and β are included. Inclusion of the $Y(kk', l')$ parameters then lowers the r.m.s. deviation to 45 - 55 cm^{-1} . Only the latter results are given in Tables I and IV.

A. Nd^{3+} in LaCl_3

About 70 energy levels of Nd^{3+} in LaCl_3 have been identified by Carlson and Dieke¹⁰ and Varsanyi and Dieke.¹¹ The simultaneous determination by Eisenstein⁶ of both the electrostatic and crystal field parameters makes it possible to compute the crystal field shifts of the electrostatic energy levels. These are given in Table I. They vary considerably, from 0 - 50 cm^{-1} , and are of the same order of magnitude as the expected r.m.s. deviation. Thus, it is absolutely necessary that these shifts be taken into account. Since a calculation equivalent to that of Eisenstein is not available for any other Nd^{3+} crystal, the present calculations were carried out only for Nd^{3+} in LaCl_3 .

Even though all of the crystal field components have been observed for only 17 levels, all 22 levels fit by Eisenstein were used in the final calculation. The uncertainty in the centers of gravity of these 5 levels is probably not greater than 10 cm^{-1} which is still considerably less than the r.m.s. deviation. Since the values of the parameters $Y(kk', l')$ are frequently determined primarily by the

positions of only those 3 or 4 levels having large angular matrix elements, it is desirable to include as many levels as possible in the least squares fit. Until the r.m.s. deviation becomes quite small, fitting an approximate position of one or more levels is frequently preferable to excluding them completely. A case in point is the $^4S_{3/2}$ level which experimentally lies below the $^4F_{7/2}$. The calculations of Eisenstein gave the wrong order and a deviation of 250 cm^{-1} for the $^4S_{3/2}$. Addition of α , β and $Y(22,3)$ reduced the deviation of the $^4S_{3/2}$ by a factor of 2 but the order remained incorrect. When $Y(22,1)$ was added, however, the order of the 2 levels was interchanged and both levels fit within a few cm^{-1} . The angular matrix element of $Y(22,1)$ for the 4S term is 6.5×10^{-2} , much larger than for any other term.⁹ Therefore, a $Y(22,1)$ value of about 3000 will shift the energy of the $^4S_{3/2}$ by about 200 cm^{-1} but have a much smaller effect on most other levels. The position of this level is thus an important factor in determining the value of $Y(22,1)$ and it is possible to get quite different values for this parameter if the $^4S_{3/2}$ is excluded.

Unfortunately, the situation is seldom so straightforward. In Er^{3+} the $^4S_{3/2}$ fits quite well in the calculation of Eisenstein⁵ and its position is not appreciably changed by the inclusion of several configuration interaction parameters. In this case, the other parameters seem to be able to compensate for the large effect of $Y(22,1)$. This fact is at least partly accounted for by the increased deviation from LS coupling in the case of Er^{3+} . It is impossible to make large changes in the calculated energy of one level without corresponding changes in several others.

By comparing his calculated positions of the ${}^2K_{15/2}$ level with that given by Richman and Wong¹² for Nd^{3+} in $LaBr_3$, Eisenstein concluded that the experimental positions of the 2K levels may lie 1500 - 3000 cm^{-1} from the calculated positions. In view of the fact that the positions resulting from the present calculation are less than 50 cm^{-1} from those calculated by Eisenstein, this seems very unlikely. However, the separation between the calculated positions of the ${}^2K_{13/2}$ and ${}^2G_{7/2}$ is only 10 cm^{-1} and that between the ${}^2K_{15/2}$ and ${}^2G_{9/2}$ is 75 cm^{-1} . Therefore, the change of 40 - 50 cm^{-1} in the positions of the 2K levels may have considerable influence on the crystal field levels of the ${}^2G_{7/2}$ and the ${}^2G_{9/2}$. This will be reflected in the crystal field shifts of these levels, with the result that the "free ion" levels fit in the present calculation may be in considerable error. This problem can be resolved only by an iterative procedure or a complete simultaneous diagonalization of all of the relevant matrices.

Over half of the final r.m.s. deviation of $\pm 46 cm^{-1}$ is accounted for by only 2 levels, ${}^2P_{1/2}$ and ${}^2(P,D)_{3/2}$. While the largest of these deviations is not appreciably outside of the expected limits of $\pm 2\sigma$, the results are somewhat suspicious. Therefore, a calculation was made, in which all three of the levels near 21,000 cm^{-1} were excluded from the fitting process. The fit was only slightly improved, but the deviation of the ${}^2P_{1/2}$ was reduced by a factor of 2 and the ${}^2G_{9/2}$ and ${}^2G_{11/2}$ were only slightly changed. But the ${}^2(P,D)_{3/2}$ deviation was increased from 84 cm^{-1} to 114 cm^{-1} . Thus it seems that this may be the questionable level and not the ${}^2P_{1/2}$. The fact that the ${}^2(P,D)_{3/2}$ has a crystal field shift over twice as large as that of any

other level also makes its assignment somewhat doubtful. There are other crystal field levels which, if assigned to the ${}^2(P,D)_{3/2}$, would result in a smaller deviation. But then the present ${}^2(P,D)_{3/2}$ levels must be reassigned. Such changes in the assignments of any of the levels in this region will probably result in changes in the positions of several "free ion" levels. The resolution to this point must also await the results of a complete crystal field calculation.

The present results are compared with those of Eisenstein in Fig. 1. Although, the changes in the lower levels are small, the shifts in some of the upper levels which have not been observed are quite large. The parameter values giving the smallest value of σ are recorded in Table II, along with those of Pr^{2+} for comparison. The addition of more parameters does not bring about any further reduction in σ . Table III contains the eigenvectors for Nd^{3+} .

B. Er^{3+} in LaCl_3

Experimental work on Er^{3+} in LaCl_3 has been reported by Dieke and Singh¹³ and Varsanyi and Dieke.¹⁴ A complete calculation was carried out by Eisenstein⁵. In this case, the crystal field shifts are generally much smaller than in Nd^{3+} . The only large shifts are for the ${}^4G_{5/2}$, ${}^2P_{1/2}$ and ${}^2L_{17/2}$, none of which have been observed experimentally. The calculation of Eisenstein puts the ${}^4G_{5/2}$ and ${}^2P_{1/2}$ only 10 cm^{-1} apart. Thus, the crystal field shifts of these levels may vary considerably with slight changes in the parameters.

By using the assignments of Eisenstein, it is possible to obtain a significant reduction in the r.m.s. deviation when the parameters α and β are included, but there is no further reduction on the addition of the parameters $Y(kk', l')$. In the latter case, however, the calculated order of the ${}^2K_{15/2}$ and ${}^2G_{9/2}$ levels is opposite that of Eisenstein. Since the original assignments of these two levels by Varsanyi and Dieke¹⁴ were reversed by Eisenstein in order to obtain better agreement with his calculations, it was decided to omit these levels from the calculation. When this was done, the r.m.s. deviation using only α and β was further decreased and an excellent fit was possible when $Y(22,1)$ was added. If these two levels are excluded from the fitting procedure their order is always in agreement with the original assignment of Varsanyi and Dieke. Therefore the assignments of the ${}^2K_{15/2}$ and ${}^2G_{9/2}$ made by Eisenstein were reversed in the final calculation recorded in Table IV. Due to the change in assignment the centers of gravity which were fit are not strictly correct. The errors are probably within the accuracy of the calculation, however.

The r.m.s. deviation of 20 levels below 37000 cm^{-1} is $\pm 47 \text{ cm}^{-1}$, and there are no levels which deviate by much more than this. We can now consider the higher levels observed by Varsanyi and Dieke which were not assigned by Eisenstein. The center of gravity of any 4 of the 5 levels labeled U by Varsanyi and Dieke is in good agreement with the calculated position of the ${}^4D_{7/2}$. Since the calculated position of the ${}^4D_{5/2}$ is 600 cm^{-1} lower it seems unlikely that the extra level belongs to the ${}^4D_{5/2}$. A complete

crystal field calculation is necessary to resolve this problem, however. The calculated position of the ${}^4I_{11/2}$ is only 18 cm^{-1} from the center of gravity of the V and W levels of Varsanyi and Dieke. Since there is no other calculated level in this region these must be identified as the crystal field components of the ${}^2I_{11/2}$ even though the agreement with the splitting calculated by Eisenstein is poor. The X levels of Varsanyi and Dieke probably belong to the ${}^2I_{17/2}$. If they are the lowest two components and the total splitting calculated by Eisenstein is assumed to be correct, the difference between theory and experiment is about 110 cm^{-1} . This deviation is much larger than any of the others, but it could probably be reduced considerably if an accurate center of gravity were known and included in the fitting procedure.

The present work is compared with that of Eisenstein in Fig. 2. Here again, the large differences between the two calculations are generally in the higher levels, many of which have not been observed. The final parameter values for Er^{3+} are given in Table II. Additional parameters produce no further decrease in σ . The eigenvectors for Er^{3+} are recorded in Table V. In some cases they are considerably different than those given by Wybourne.¹⁵

C. Er^{3+} in LaF_3

The energy levels of Er^{3+} in a matrix of LaF_3 have recently been given by Krupke and Gruber.⁸ It is interesting to confirm the previous results by comparison with Er^{3+} in a different crystal. No complete calculation from which to derive the crystal field shifts

is available for Er^{3+} in LaF_3 . Since the crystal field shifts were generally small in LaCl_3 it is probably safe to assume that, within the limits of the present calculation, they are also negligible in LaF_3 . The experimental levels given in Table IV are thus those of Krupke and Gruber.

Using the assignments given by Krupke and Gruber, it was impossible to obtain any improvement in the fit on the addition of α and β . Furthermore the parameters α and β were both opposite in sign and quite different in magnitude from those obtained for Er^{3+} in LaCl_3 . The level at 32922.2 which deviated by nearly 400 cm^{-1} in the calculation of Krupke and Gruber was only slightly improved. When this level was excluded from the fit the r.m.s. deviation was reduced by 60 cm^{-1} and it was immediately obvious that this level must be assigned to the ${}^2K_{13/2}$ rather than the ${}^4G_{5/2}$. Krupke and Gruber have stated that such a change is not in conflict with their data.¹⁶ With this new assignment, an r.m.s. deviation of $\pm 83 \text{ cm}^{-1}$ was obtained on the addition of α and β and the final value of $\pm 54 \text{ cm}^{-1}$ resulted from the addition of $\Upsilon(22,1)$. Since all of the crystal field components of the ${}^2K_{13/2}$ were not observed, there is undoubtedly some error in the experimental energy quoted in Table IV. This is probably not enough to have an appreciable effect on the final results. As in the previous case, no further reduction of σ was possible when additional parameters were added. The results are given in Tables II and IV.

D. Er³⁺ in Er(C₂H₅SO₄)₃·9H₂O

A similar calculation, assuming zero crystal field shifts was also carried out for Er³⁺ in Er(C₂H₅SO₄)₃·9H₂O. In order to obtain sufficient levels for such a fit it is necessary to use the combined data of Erath¹⁷ and Hufner.¹⁸ The experimental levels below 27000 cm⁻¹ in Table IV are those of Erath at 77°K and those above 27000 cm⁻¹ are taken from the work of Hufner. Some of the latter measurements were made at 4.2°K and some at 77°K. The discrepancy between the two values of the ⁴G_{11/2} which appears in the tables of both Erath and Hufner is 5.4 cm⁻¹. Thus, although the data being fit in the present calculation are not as consistent as in the previous calculations, the discrepancies are considerably smaller than the final r.m.s. deviation and should not have any significant effect on the final results.

For the levels observed in erbium ethylsulfate, the fit is quite good. The levels which the calculations of Kahle¹⁹ put in the wrong order now fit very well. The additional levels observed by Hufner only in ErCl₃·6H₂O, however, fit very poorly. The ²P_{1/2} deviates by 684 cm⁻¹ and there is no satisfactory correspondence between the observed and calculated levels above 39000 cm⁻¹. The only exception is the ⁴D_{7/2} which fits very well and was included in the calculations. Hufner attributes the large deviations to interaction between the configurations 4f¹¹ and 4f¹⁰5d. But these configurations are of opposite parity and, therefore, cannot interact via the Coulomb interaction, e²/r_{ij} considered here. The configurations 4f¹¹ and 4f¹⁰5d can interact via the crystal field. This leads to a shielding

of the crystal field parameters which, in intermediate coupling, will be different for each J-level.²⁰ It is unlikely that these changes in the crystal field splitting will shift the centers of gravity by thousands of cm^{-1} . Furthermore, since the major part of electrostatic configuration interaction effects have now been included in it is unlikely that the inclusion of additional parameters will cause shifts of more than a few hundred cm^{-1} . If the upper two levels are regarded as crystal field components of the same level, there is rough agreement with the calculated position of the ${}^2I_{11/2}$. This also agrees quite well with the tentative assignment of the ${}^2I_{11/2}$ in LaCl_3 . The levels at 38850 and 39350 don't seem to correspond to any of the calculated levels, however.

III. CONCLUSIONS

From the results in Table II, it is now possible to make some comparison of the configuration interaction effects for $4f^3$ configurations in various ions. The parameters α and β are considerably smaller in Nd^{3+} than in Pr^{2+} , while the "nonlinear" parameters are nearly the same for the two ions. This indicates that, whereas interaction with configurations differing from $4f^3$ in the quantum numbers of two electrons is much less in Nd^{3+} than in Pr^{2+} , interaction with configurations differing from $4f^3$ by only one electron is not appreciably different in the two ions. From the positive sign of $Y(22,1)$ in Nd^{3+} , we may conclude that interaction with configurations involving the removal of a p electron from a filled shell dominates over interaction between $4f^3$ and $4f^2np$.

For Er^{3+} the parameters α and β are much larger than for Nd^{3+} , although still somewhat smaller than those of Pr^{2+} . $Y(22,1)$ is of the same magnitude as in Nd^{3+} but of opposite sign. Thus the interaction between $4f^{11}$ and $4f^{10}n^1p$ is the dominant interaction in this case. No decrease in the r.m.s. deviation could be obtained by including $Y(22,3)$. Either this parameter is really very small or it is most sensitive to the positions of levels which were not included in the present calculations.

The variations in the Er^{3+} parameters for the various crystals cannot be deemed physically significant at the present time. For two of the crystals, the crystal field shifts were assumed to be negligible which may not actually be the case. Many of the centers of gravity were estimated from an incomplete set of crystal field components. The data on erbium ethylsulfate is the result of measurements at two different temperatures. These uncertainties in the experimental "free ion" levels may well be large enough to account for the differences in the parameters from crystal to crystal. In order to determine whether or not these differences in parameters are physically significant it would be necessary to repeat the calculations of Eisenstein for each crystal, with the inclusion of the relevant configuration interaction parameters. Until such calculations are carried out it is impossible to draw any conclusion from the variation of the parameters from crystal to crystal.

When higher levels can be included in the calculations, it may be necessary to use additional parameters of configuration interaction. This will probably result in some changes in the values obtained here,

but should not change any of the general conclusions. The present values of the configuration interaction parameters should provide a useful starting point for the analysis of the spectra of other triply ionized rare earth ions. They also provide another step in our understanding of the relative magnitudes of various mechanisms of configuration interaction.

The results also show quite clearly that the practice of assigning "free ion" energy levels by comparison with a least squares fit of only 4 parameters may occasionally lead to erroneous assignments. If reliable assignments are to be made, either an experimental determination of J values or a more complete calculation including the effects of configuration interaction may frequently be necessary.

Table I. Experimental and Calculated "Free Ion" Energy Levels of Nd³⁺ in LaCl₃

Level	Crystal field shift ^a	Experimental "free ion" energy	Calculated energy	E _{calc.} - E _{exp.}
⁴ I _{9/2}	0.00	1870.00	1875.87	5.87
⁴ I _{11/2}	7.82	1873.71	1868.97	-4.74
⁴ I _{13/2}	8.90	3855.48	3853.58	-1.90
⁴ I _{15/2}	14.31	5903.38	5916.05	12.67
⁴ F _{3/2}	9.43	11283.00	11259.85	-23.15
⁴ F _{5/2}	7.84	12311.19	12300.07	-21.12
² H _{9/2}	4.85	12463.67	12518.30	54.63
⁴ F _{7/2} ^b	10.78	13282.42	13285.12	2.70
⁴ S _{3/2} ^b	13.16	13369.59	13373.91	4.32
⁴ F _{9/2}	9.07	14567.03	14578.43	11.40
² H _{11/2}	10.22	15780.88	15814.19	33.31
⁴ G _{5/2}	-0.71	16980.14	16960.59	-19.55
(² G, ⁴ G) _{7/2}	23.04	-	17088.03	-
² K _{13/2}	0.60	-	18841.70	-
⁴ G _{7/2}	19.42	18865.82	18852.90	-12.92
² G _{9/2}	17.14	19279.55	19295.35	15.80
² K _{15/2}	-13.37	-	20820.54	-
⁴ G _{9/2}	18.62	20901.12	20886.70	-14.42
² (P,D) _{3/2}	54.23	20974.01	21058.48	84.47
⁴ G _{11/2}	25.09	21271.50	21297.49	25.99
² P _{1/2}	8.96	23059.50	22958.23	-101.27
² D _{5/2}	13.43	23625.68	23655.16	29.48
² (P,D) _{3/2}	4.33	26005.52	26017.34	11.82
⁴ D _{3/2}	1.32	27826.49	27805.58	-20.91

Table I. (Cont'd.)

Level	Crystal field shift	Experimental "free ion" energy	Calculated energy	$E_{\text{calc.}} - E_{\text{exp.}}$
$^2D_{5/2}$	9.55	27983.10	27983.10	-
$^2I_{11/2}$	2.67	-	28292.28	-
$^4D_{1/2}$	17.61	28350.44	28372.75	22.31
$^2L_{15/2}$	11.88	-	28891.12	-
$^2I_{13/2}$	8.81	-	29664.44	-
$^4D_{7/2}$	13.50	-	30029.84	-
$^2L_{17/2}$	14.16	-	30360.93	-

^aCrystal field shifts have been normalized so that the shift of the ground state is zero.

^bThe order of the $^4F_{7/2}$ and $^4S_{3/2}$ is opposite that calculated by Eisenstein.

Table II. Parameter Values for Pr^{2+} , Nd^{3+} and Er^{3+} (in cm^{-1})

Parameter	Pr^{2+} (free ion)	Nd^{3+} (in LaCl_3)	Er^{3+} (in LaCl_3)	Er^{3+} (in LaF_3)	Er^{3+} (in $\text{Er}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$)
E^0	15030.	13764.	21540.	21564.	21535.
E^1	4863.4	4912.1	6911.8	6924.1	6957.6
E^2	19.79	22.93	32.35	32.65	32.52
E^3	410.1	467.5	642.3	650.72	648.27
ζ	665.0	878.6	2366.5	2361.4	2353.4
α	31.65	1.24	17.89	17.00	17.49
β	-839.7	-148.2	-742.9	-609.0	-690.3
γ	-3164.	-	-	-	-
$Y(22, 1)$	6250	3150.	-4250.	-4280.	-4560.
$Y(42, 1)$	6150.	-	-	-	-
$Y(44, 1)$	2100	-	-	-	-
$Y(22, 3)$	-14280.	-13840.	-	-	-
$Y(44, 3)$	-4380.	-	-	-	-
No. of Levels	37	22	20	21	21
σ	$\pm 29 \text{ cm}^{-1}$	$\pm 46 \text{ cm}^{-1}$	$\pm 47 \text{ cm}^{-1}$	$\pm 54 \text{ cm}^{-1}$	$\pm 50 \text{ cm}^{-1}$

Table III. Eigenvectors and g Values for Nd³⁺ in LaCl₃

Energy	Eigenvectors						g	
	⁴ D	² P	⁴ S	⁴ D	⁴ F	² P		(20) ² D
J = 1/2								
22958.23	0.2662	0.9639						0.619
28372.75	-0.9639	0.2662						0.049
J = 3/2								
11259.85	0.0466	0.0118	-0.9711	0.0564	-0.2192	0.0582		0.426
13373.91	0.9715	0.0153	0.0694	0.2222	-0.0422	0.0030		1.959
21058.48	0.1949	-0.1361	-0.1920	-0.6512	0.6821	-0.1312		1.064
26017.34	0.1243	-0.1098	0.1230	-0.7020	-0.6613	0.1650		1.080
27805.58	-0.0229	-0.9059	-0.0023	0.1482	-0.1068	-0.3814		1.141
33029.41	-0.0104	-0.3852	0.0111	0.0924	0.1902	0.8981		0.864
J = 5/2								
12300.07	⁴ D	⁴ F	⁴ G	(20) ² D	(21) ² D	(10) ² F	(21) ² F	
12300.07	-0.0028	0.9882	-0.0195	0.1448	-0.0168	-0.0269	-0.0315	1.032
16960.59	-0.0083	0.0242	0.9935	-0.0019	-0.0154	0.0761	0.0794	0.574
23655.16	-0.0086	-0.1445	0.0088	0.9874	0.0584	-0.0214	-0.0113	1.197
27983.10	-0.9011	-0.0075	-0.0280	0.0187	-0.4128	0.0876	0.0939	1.334
34140.83	-0.4306	0.0072	0.0490	-0.0596	0.8207	-0.2096	-0.3018	1.184
38998.26	-0.0465	0.0423	-0.0958	0.0038	0.3900	0.5482	0.7309	0.908
67589.83	-0.0182	-0.0008	0.0134	-0.0111	0.0046	-0.8006	0.5987	0.857

Table III. (Continued)

Energy		Eigenvectors						g	
J = 7/2		4_D	4_F	4_G	$(10)^2_F$	$(21)^2_F$	$(20)^2_G$	$(21)^2_G$	
	13285.12	-0.0031	-0.9662	-0.0323	0.0287	0.0390	0.1972	-0.1554	1.216
	17088.03	-0.0022	-0.2126	0.6360	0.0158	0.0164	-0.5630	0.4824	0.943
	18852.90	-0.0074	0.1394	0.7677	0.0461	0.0533	0.4881	-0.3845	0.953
	30029.84	0.9946	-0.0064	0.0135	-0.0852	-0.0562	0.0101	0.0004	1.426
	40299.27	-0.0942	-0.0409	0.0641	-0.5239	-0.8398	0.0702	0.0248	1.144
	47355.47	0.0042	-0.0088	0.0226	0.0400	-0.0987	-0.6310	-0.7680	0.892
66590.63	0.0422	0.0036	-0.0127	0.8447	-0.5264	0.0517	0.0690	1.142	
J = 9/2		4_F	4_G	4_I	$(20)^2_G$	$(21)^2_G$	$(11)^2_H$	$(21)^2_H$	
	5.87	-0.0031	-0.0077	-0.9847	0.0168	-0.0148	-0.0566	0.1631	0.732
	12518.30	0.3770	0.1440	-0.1505	-0.3382	0.2798	0.2868	-0.7346	1.010
	14578.43	0.8653	-0.0406	0.0771	-0.1215	0.0787	-0.1582	0.4445	1.231
	19295.35	-0.1724	0.8694	0.0334	-0.2682	0.2543	-0.1279	0.2455	1.148
	20886.70	0.2812	0.4653	-0.0259	0.6287	-0.5017	0.0039	-0.2383	1.130
	31977.41	0.0045	0.0679	0.0042	-0.0124	-0.1062	0.9306	0.3434	0.912
46478.79	0.0154	-0.0230	0.0005	0.6350	0.7666	0.0843	0.0358	1.110	
J = 11/2		4_G	4_H	$(11)^2_H$	$(21)^2_H$	2_I			
	11868.97	0.0072	0.9948	0.0361	-0.0942	-0.0151			0.966
	15814.19	-0.2401	0.0987	-0.3662	0.8920	-0.0534			1.100
	21297.49	-0.9613	-0.0170	0.2173	-0.1683	-0.0097			1.259
	28292.28	0.0715	-0.0168	0.3629	0.1148	-0.9218			0.949
	33367.47	0.1144	0.0121	0.8281	0.3924	0.3835			1.069

Table III. (Continued)

Energy	Eigenvectors			g
	4_I	2_I	2_K	
$J = 13/2$				
3853.58	0.9977	-0.0232	0.0640	1.079
18841.70	0.0661	0.1009	-0.9927	0.935
29664.44	0.0166	0.9946	0.1022	1.076
$J = 15/2$	4_I	2_K	2_L	
5916.05	0.9931	0.1166	-0.0091	1.199
20820.54	-0.1158	0.9683	-0.2213	1.062
28891.12	-0.0170	0.2208	0.9752	0.947
$J = 17/2$	2_L			
30360.93	1.0000			1.059

Table IV. Experimental and Calculated Energy Levels of Er^{3+} in LaCl_3 , LaF_3 and $\text{Er}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$

Level	Crystal field shift ^a	LaCl_3			LaF_3			$\text{Er}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$		
		Experimental "free ion" energy	Calculated energy	$E_{\text{calc}} - E_{\text{exp.}}$	Experimental energy	Calculated energy	$E_{\text{calc}} - E_{\text{exp.}}$	Experimental energy	Calculated energy	$E_{\text{calc}} - E_{\text{exp.}}$
$^4\text{I}_{15/2}$	0.00	0.00	23.35	23.35	0.0	14.1	14.1	0.00	-6.7	-6.7
$^4\text{I}_{13/2}$	-0.01	6481.58	6485.36	3.78	6480.8	6458.3	-22.5	-	6413.0	-
$^4\text{I}_{11/2}$	0.64	10110.74	10082.67	-28.07	10123.1	10069.1	-54.0	-	10029.9	-
$^4\text{I}_{9/2}$	0.68	12350.60	12295.76	-54.84	12350.7	12315.0	-35.7	12366.5	12299.3	-67.2
$^4\text{F}_{9/2}$	1.52	15174.05	15222.07	48.02	15235.7	15284.6	48.9	15207.2	15252.5	45.3
$^4\text{S}_{3/2}$	0.66	18290.62	18283.77	-6.25	18353.3	18347.2	-6.1	18326.8	18333.8	7.0
$^2\text{H}_{11/2}$	-1.20	19035.63	19069.35	33.72	19117.5	19192.8	75.3	19087.1	19156.9	69.8
$^4\text{F}_{7/2}$	2.58	20406.91	20438.30	31.38	20492.1	20524.6	32.5	20457.3	20477.8	20.5
$^4\text{F}_{5/2}$	1.39	22066.23	22068.98	2.75	22161.9	22163.8	1.9	22121.6	22117.7	-3.9
$^4\text{F}_{3/2}$	1.53	22407.81	22357.15	-50.66	22494.4	22445.6	-48.8	22460.9	22408.1	-52.8
$^2\text{H}_{9/2}$	-0.63	24457.32	24412.64	-44.68	24526.8	24484.9	-41.9	24515.4	24467.9	-47.5
$^4\text{G}_{11/2}$	-3.21	26262.58	26290.31	27.73	26368.5	26465.5	97.0	26348.1	26389.8	41.7
$^2\text{G}_{9/2}$	2.10	27219.24	27216.13	-3.11	27412.2	27431.1	18.9	27353.	27315.9	-37.
$^2\text{K}_{15/2}$	2.20	27497.60	27550.66	53.06	-	27675.3	-	27653.	27683.4	30.
$^2\text{G}_{7/2}$	2.99	27878.98	27837.88	-41.10	28081.5	28013.7	-67.8	27963	27969.0	6.
$^2\text{P}_{3/2}$	-4.11	31389.03	31434.79	45.76	31501.0	31556.8	55.8	31473.0	31526.1	53.1
$^2\text{K}_{13/2}$	1.40	32855.53	32803.66	-51.87	32922.2	32923.3	1.1	32953.	32918.8	-34.

Table IV. (Continued)

Level	Crystal field shift	LaCl ₃			LaF ₃			Er(C ₂ H ₅ SO ₄) ₃ ·9H ₂ O		
		Experimental "free ion" energy	Calculated energy	$E_{\text{calc}} - E_{\text{exp.}}$	Experimental energy	Calculated energy	$E_{\text{calc}} - E_{\text{exp.}}$	Experimental energy	Calculated energy	$E_{\text{calc}} - E_{\text{exp.}}$
⁴ G _{5/2}	21.36	-	33130.75 ^b	-	-	33386.4	-	33243.	33246.0	3.
² P _{1/2} ^b	-59.68	-	33178.37 ^b	-	-	33311.6	-	32623. ^{d,e}	33306.5	684.
⁴ G _{7/2}	1.97	33836.21	33807.71	-28.50	33994.7	33977.3	-17.4	33923.	33891.6	-31.
² D _{5/2}	0.23	34647.99	34636.08	-11.90	34838.3	34811.2	-27.1	34803.	34768.1	-35.
² H _{9/2} ^c	1.07	36331.92	36383.25	51.33	36424.3	36445.2	41.9	36363.	36408.3	45.
⁴ D _{5/2}	-.25	-	38215.70	38610.0	38610.0	38584.7	-25.3	38543	38474.3	-69.
⁴ D _{7/2}	2.20	-	38846.92		39313.6	39294.0	-19.6	39073. ^d	39115.2	42.
² I _{11/2}	-0.64	-	40764.32		40976.2	40976.2	-	38850. ^{d,e}	40971.3	
² L _{17/2}	36.08	-	41366.54		-	41609.7	-	39350. ^{d,e}	41576.2	
² D _{3/2}	1.05	-	41944.98		-	42230.4	-	40990. ^{d,e}	42110.4	
⁴ D _{3/2} ^b	1.47	-	42598.81 ^b		-	42857.5	-	41190. ^{d,e}	42768.9	
² I _{13/2} ^b	7.81	-	43376.19 ^b		-	43560.5	-		43541.1	

^aCrystal field shifts have been normalized so that the shift of the ground state is zero.

^bThe order of these two levels is inverted from that calculated with only the Slater parameters.

^cThis level was called ⁴D_{9/2} by Krupke and Gruber in LaF₃ and ⁴G_{9/2} by Hufner in the ethylsulfate. The eigenvector in LaCl₃ shows nearly equal contributions from all three terms.

^dLevels observed only in ErCl₃·6H₂O at 77° K.

^eLevels not included in the fitting procedure.

Table V. Eigenvectors for Er^{3+} in LaCl_3

Energy		Eigenvector							g
J = 1/2		4_D	2_P						
	33178.37	0.2906	-0.9568						0.610
	46634.31	0.9568	0.2906						0.058
J = 3/2		4_S	4_D	4_F	2_P	$(20)^2D$	$(21)^2D$		
	18283.77	0.8316	0.0434	0.2210	-0.4272	-0.2732	-0.0237		1.710
	22357.15	0.3998	-0.0001	-0.7892	0.0756	0.4601	0.0015		0.745
	31434.79	-0.3403	0.1833	-0.4971	-0.5972	-0.4582	-0.1918		1.044
	41944.98	-0.0661	0.7763	0.2325	-0.2360	0.4958	-0.1934		1.054
	42598.81	-0.1666	-0.3940	0.1136	-0.6131	0.4387	0.4855		1.090
	54842.25	0.0264	0.4546	-0.1194	0.1532	-0.2555	0.8304		0.890
J = 5/2		4_D	4_F	4_G	$(20)^2D$	$(21)^2D$	$(10)^2F$	$(21)^2F$	
	22068.98	0.0468	-0.9189	0.0380	-0.3580	-0.1312	-0.0396	-0.0716	1.052
	33130.75	-0.0179	-0.0310	-0.9615	0.1097	0.0884	0.1474	0.1808	0.599
	34636.08	0.3805	0.3704	0.0296	0.7536	-0.3849	0.0197	-0.0264	1.201
	38215.70	-0.6661	0.1015	0.1351	0.5318	0.4867	0.0317	0.0835	1.261
	48718.19	0.6212	-0.0635	0.1418	0.0690	0.6892	0.1807	0.2785	1.216
	63184.66	-0.1460	-0.0559	0.1807	-0.0604	-0.3385	0.3930	0.8186	0.900
94629.77	0.0413	0.0101	-0.0470	0.0253	0.0198	-0.8878	0.4547	0.857	

Table V. (Continued)

Energy		Eigenvector							g
J = 7/2		4D	4F	4G	$(10)^2F$	$(21)^2F$	$(20)^2G$	$(21)^2G$	
	20438.30	0.0111	0.9603	0.0330	0.0434	0.0537	0.2140	-0.1613	1.213
	27837.88	-0.0567	-0.2011	0.6557	-0.1360	-0.1438	0.5026	-0.4844	0.956
	33807.71	0.0340	-0.1631	-0.7304	0.0401	0.0301	0.5264	-0.3990	0.950
	38846.92	0.9798	-0.0345	0.0926	0.1470	0.0864	0.0310	-0.0098	1.417
	55540.07	0.1759	0.0976	-0.1587	-0.5730	-0.7664	-0.1337	-0.0262	1.144
	65055.84	0.0063	0.0073	-0.0394	-0.0326	0.1709	-0.6318	-0.7543	0.896
98040.21	0.0664	0.0016	-0.0141	-0.7918	0.5928	0.0806	0.1023	1.140	
J = 9/2		4F	4G	4I	$(20)^2G$	$(21)^2G$	$(11)^2H$	$(21)^2H$	
	12295.76	0.3592	0.0122	-0.7267	0.2796	-0.2264	0.1948	-0.4188	0.894
	15222.07	0.7673	0.0926	0.5119	0.2905	-0.2212	-0.0013	0.0855	1.141
	24412.64	0.4953	-0.2609	-0.3466	-0.4321	0.3939	-0.2604	0.3960	1.078
	27216.13	0.0134	-0.8879	0.2258	-0.0019	0.0452	0.1007	-0.3850	1.108
	36383.25	0.1898	0.3532	0.1946	-0.4851	0.3980	0.2900	-0.5688	1.030
	47638.85	0.0007	0.0850	0.0302	-0.0852	-0.1638	-0.8804	-0.4274	0.918
69199.49	0.0269	-0.0529	-0.0033	-0.6389	-0.7466	0.1578	0.0778	1.105	

Table V. (Continued)

Energy		Eigenvector					g
J = 11/2		4_G	4_I	$(11)^2_H$	$(21)^2_H$	2_I	
	10082.67	0.1154	0.9074	-0.1081	-0.3841	0.0634	0.989
	19069.35	-0.6016	0.3862	0.1433	-0.6822	-0.0551	1.138
	26290.31	0.7735	0.1621	0.3222	-0.5207	-0.0236	1.197
	40764.32	-0.1101	-0.0321	0.5466	0.1275	0.8196	0.980
50758.31	0.1201	-0.0108	-0.7518	-0.3157	0.5662	1.040	
J = 13/2		4_I	2_I	2_K			
	6485.36	0.9955	0.0318	-0.0893			1.078
	32803.66	0.0750	0.3125	0.9470			0.948
43376.19	0.0580	-0.9494	0.3087			1.063	
J = 15/2		4_I	2_K	2_L			
	23347.55	0.9852	-0.1702	-0.0173			1.196
	27550.66	0.1694	0.9560	0.2396			1.063
47558.47	-0.0242	-0.2390	0.9707			0.948	
J = 17/2	41366.54	2_L					1.059

FOOTNOTES AND REFERENCES

- *
1. Based on work performed under the auspices of the U. S. Atomic Energy Commission.
1. W. A. Runciman and B. G. Wybourne, J. Chem. Phys. 31, (1149)(1959).
 2. J. S. Margolis, J. Chem. Phys. 35, 1367 (1961).
 3. B. R. Judd, Proc. Roy. Soc. A 251, 134 (1959).
 4. J. C. Eisenstein, International Conference on Paramagnetic Resonance, Jerusalem, 1962, edited by W. Low (Academic Press, Inc., New York, 1963).
 5. J. C. Eisenstein, J. Chem. Phys. 39, 2128 (1963).
 6. J. C. Eisenstein, J. Chem. Phys. 39, 2134 (1963).
 7. K. Rajnak and B. G. Wybourne, Phys. Rev. 132, 280 (1963), 134, A596 (1964).
 8. W. F. Krupke and J. B. Gruber, J. Chem. Phys. 41, 1225 (1964).
 9. K. Rajnak, J. Opt. Soc. Am. (to be published).
 10. E. H. Carlson and G. H. Dieke, J. Chem. Phys. 34, 1602 (1961).
 11. F. Varsanyi and G. H. Dieke, J. Chem. Phys. 33, 1616 (1960).
 12. I. Richman and E. Y. Wong, J. Chem. Phys. 37, 2270 (1962).
 13. G. H. Dieke and S. Singh, J. Chem. Phys. 35, 555 (1961).
 14. F. Varsanyi and G. H. Dieke, J. Chem. Phys. 36, 2951 (1962).
 15. B. G. Wybourne, J. Chem. Phys. 34, 279 (1961).
 16. W. F. Krupke and J. B. Gruber, J. Chem. Phys. (to be published).
 17. E. H. Erath, J. Chem. Phys. 34, 1985 (1961).
 18. S. Hüfner, Z. Physik, 168, 74 (1962).
 19. H. G. Kahle, Z. Physik, 161, 486 (1961).
 20. K. Rajnak and B. G. Wybourne, J. Chem. Phys. 41, 565 (1964).

FIGURE CAPTIONS

Fig. 1. "Free ion" energy levels of Nd^{3+} : (a) Calculated using the parameters of Eisenstein; (b) Results of present calculations; (c) Experimental levels.

Fig. 2. "Free ion" energy levels of Er^{3+} : (a) Calculated using the parameters of Eisenstein; (b) Results of present calculations; (c) Experimental levels.

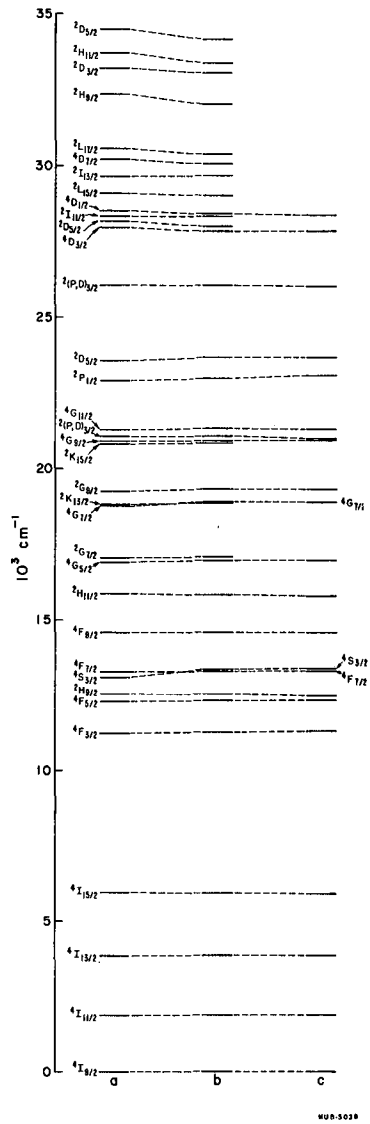


Fig. 1

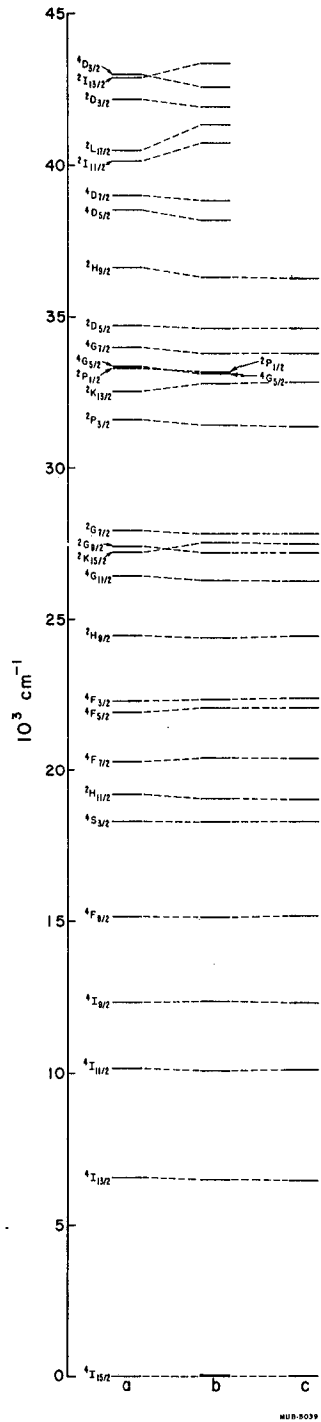


Fig. 2

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

