

Correlation-crystal-field analysis of the ${}^2H(2)_{11/2}$ multiplet of Nd^{3+}

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Orthogonal correlation-crystal-field (CCF) operators for the f^N configuration have been discussed in an earlier paper, with emphasis on the anomalous multiplets 3K_8 of Ho^{3+} and ${}^6I_{17/2}$ of Gd^{3+} . In those cases the $\mathbf{g}_3^{(6)}$ operator, which is a major component of the sixth-rank spin-correlated crystal-field operator, was found to be useful. In this paper we turn our attention to the ${}^2H(2)_{11/2}$ multiplet of Nd^{3+} . The one-electron crystal-field parametrization consistently *underestimates* the splitting of this multiplet, and several possible corrections have recently been suggested in the literature. We show, by analyzing the spectrum of Nd^{3+} in several host crystals, that the addition of the fourth-rank orthogonal CCF operator $\mathbf{g}_{10A}^{(4)}$ to the Hamiltonian removes the anomaly. Our fits are in qualitative agreement with *ab initio* calculations of CCF effects for lanthanide ions.

I. INTRODUCTION

Crystal-field models for paramagnetic ions have recently been reviewed,¹ with emphasis on the f^N configuration. The standard parametrization scheme assumes that each f electron interacts independently with the crystal potential. This has been a very successful approach, but evidence has built up that correlation has an observable effect on the spectra. Extensions of the crystal-field parametrization to include the effects of electron correlation have been discussed in detail in Ref. 1 and other recent publications (see Ref. 2).

The term *crystal field* is often misunderstood. We consider the crystal field to include any interaction that breaks the spherical symmetry of the ion. The obvious potential from the charges of the other ions in the crystal is sometimes erroneously assumed to provide the dominant, even the entire, effect. However, it is now well established that quantum-mechanical effects arising from wave-function overlap play a major role.¹

The crystal-field model has provided a useful way to deal with spectroscopic data because we can reduce the experimentally observed energy levels to a set of *parameters*. Subsequently, we can search for patterns in the parameter sets, and attempt to explain the results by *ab initio* calculations. We emphasize that the parameter fitting approach makes only minimal assumptions about the physical origin of the crystal-field interaction.

The usual one-electron crystal-field parametrization for the f^N configuration of lanthanide and actinide ions is commonly defined as^{1,2}

$$\mathcal{H}_{\text{CF}} = \sum_{KQ} B_Q^K C_Q^{(K)}, \quad (1)$$

where

$$C_Q^{(K)} = \sum_i c_Q^{(K)}(i) \quad (2)$$

and $c_Q^{(K)}(i)$ is a spherical tensor operator for the i th f electron. The orbital angular momentum label K runs over the range 0, 2, 4, 6, but the $K=0$ term does not

affect the splitting of the f^N configuration and can be ignored for our purposes. The form of Eq. (2), a sum of one-electron operators, makes it clear that the standard crystal-field parametrization does not take into account many-electron (correlation) effects.

As discussed in Refs. 1–5 there is considerable evidence that *correlation* between f electrons has observable effects on the crystal-field splitting. In many cases, the splitting of a few multiplets remains poorly fitted when the crystal-field parameters are optimized using all the observed energy levels. When a similar pattern exists for the same ion in several different host crystals [which is the case for the ${}^2H(2)_{11/2}$ multiplet of Nd^{3+} considered here^{6–13}] it is clear that the Hamiltonian needs to be extended beyond the one-electron crystal field. Correlation-induced modifications to the Coulomb interaction in the f^N configuration are routinely parameterized,^{9,11} so it seems reasonable that correlation will also play a role in the crystal-field interaction.

The most obvious spin-independent parametrization of two-electron interactions may be written²

$$\mathcal{H}_{\text{CCF}} = \sum_{k_1 k_2 K} B_Q^K(k_1 k_2) \sum_{i>j} [u^{(k_1)}(i)u^{(k_2)}(j)]_Q^{(K)}, \quad (3)$$

where CCF stands for correlation-crystal field, the $u^{(k)}$ are unit tensor operators and i and j label the f electrons. The quantum numbers k_1 and k_2 can range from 0 to 6, including odd integers, and K can run through the even integers from 0 to 12 (strictly, the restriction for K to be even is a result of superposition model assumptions¹). Note that this parameter set includes the one-electron crystal field (if k_1 or $k_2=0$) and the two-body Coulomb operators (if $K=0$). Judd³ has given an alternative parametrization in terms of orthogonal operators which have well-defined transformation properties under the “parentage” groups Sp_{14} , R_7 , and G_2 used by Racah to label states of the f^N configuration. In Judd’s notation the orthogonal CCF is written^{2,3}

$$\mathcal{H}_{\text{OCCF}} = \sum_{iKQ} G_{iQ}^K g_i^{(K)}. \quad (4)$$

As in Eq. (3), K runs through the even integers from 0 to 12, Q is restricted by symmetry, and the number of operators varies with K . The $\mathbf{g}_i^{(K)}$ operators with $K=0$ correspond to Coulomb interactions and those with $i=1$ to one-electron operators, in fact $\mathbf{g}_1^{(K)} \equiv \mathbf{U}^{(K)}$. Clearly one can transform between the two parameter sets defined by Eqs. (3) and (4).

Judd's CCF operators have several advantages. Unlike the operators in Eq. (3) they are orthogonal over the f^N configuration. Also, the well-defined transformation properties under the groups Sp_{14} , R_7 and G_2 give us more scope for developing group-theoretical arguments concerning contributions to the parameters (see Sec. V).

In previous work² we corrected some residual nonorthogonality in Judd's operators, defining $\mathbf{g}_2'^{(K)}$ operators which are orthogonal to the $\mathbf{g}_1^{(K)}$. We also showed that the spin-correlated crystal-field (SCCF) operators could be written as a linear combination of $\mathbf{g}_1^{(K)}$, $\mathbf{g}_2'^{(K)}$, and $\mathbf{g}_3^{(K)}$. It is straightforward to see that only these operators can contribute. The SCCF is obtained by multiplying the one-electron crystal-field operators by $\mathbf{S} \cdot \mathbf{s}_i$, where \mathbf{S} and \mathbf{s}_i are operators for the total spin and the spin of the i th electron. $\mathbf{S} \cdot \mathbf{s}_i$ is a scalar in orbital space so it must transform as the irreducible representations $W=(000)$, $U=(00)$ of R_7 and G_2 . Hence, the SCCF operator must have the same W and U labels as the one-electron crystal-field operator ($\mathbf{g}_1^{(K)}$ or $\mathbf{C}^{(K)}$), namely (200) and (20). Inspection of Table III of Ref. 2 or Table I of Ref. 3 shows that only $\mathbf{g}_1^{(K)}$, $\mathbf{g}_2'^{(K)}$, and $\mathbf{g}_3^{(K)}$ fulfill this requirement.

Unfortunately it has proved difficult to determine values for CCF parameters, apart from some success with the SCCF parameters.^{2,4} There are dozens of CCF operators, too many to simply allow all the parameters to vary freely in the fits. This is in contrast to the nine parameters (α , β , γ , and six T_k), which parameterize correlation-induced modifications of the Coulomb interaction for the f^N configuration.⁹ In order to make progress the only viable approach seems to be to seek out features of the spectra that are particularly sensitive to certain operators.

In our earlier work² we analyzed the spectra of Ho^{3+} and Gd^{3+} doped into LaCl_3 . These spectra had already been fitted by Crosswhite and Newman,⁴ using the SCCF parametrization.⁵ We found that only the sixth-rank SCCF parameter, or, equivalently, G_3^6 was well determined by the experimental data, though for Gd^{3+} there were important fourth-rank contributions. In that work we emphasized close examination of the anomalous multiplets 3K_8 of Ho^{3+} and ${}^6I_{17/2}$ of Gd^{3+} . The fits to these multiplets were dramatically improved by the inclusion of the $\mathbf{g}_3^{(6)}$ operator.

Our inability to determine values for other CCF parameters from the Gd^{3+} and Ho^{3+} spectra should not be misinterpreted. Those systems were specifically selected by Judd,⁵ and subsequently by Crosswhite and Newman,⁴ as examples where the SCCF parametrization was expected to have an obvious effect. Our task is to find features of other data sets that will allow us to determine the values of other CCF operators.

Recently, Faucher and co-workers^{6,7} have made a detailed study of the ${}^2H(2)_{11/2}$ multiplet of Nd^{3+} . When a crystal-field fit is carried out for the entire spectrum, the splitting calculated for this multiplet is consistently smaller than the experimental splitting. Faucher and co-workers made various suggestions for fixing this problem, their latest being an adjustment to the reduced matrix elements of the fourth-rank crystal-field operator for this multiplet.⁷ We shall see that this adjustment is consistent with the introduction of the CCF operator $\mathbf{g}_{10,A}^{(4)}$. [There are two $\mathbf{g}_{10}^{(K)}$ operators with $K=4$, labeled A and B by Judd,³ because of a branching multiplicity from the G_2 irreducible representation (40).]

We have performed fits for Nd^{3+} in several different hosts including YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$),⁸ LaCl_3 ,⁹ LiYF_4 ,¹⁰ LaF_3 ,¹¹ NdAlO_3 ,¹² and NdODA ($\text{Na}_3[\text{Nd}(\text{C}_4\text{H}_4\text{O}_5)_3 \cdot 2\text{NaClO}_4]_3$).¹³ Most of the spectra analyzed contain over 100 crystal-field levels. Quite consistent results for the ratio of the $\mathbf{G}_{10,A}^4$ parameters to the one-electron \mathbf{B}^4 parameters are obtained.

As well as the possibility of allowing more systematic and accurate analyses of spectra, the determination of CCF parameters is a useful test of *ab initio* calculations. Ng and Newman^{14,15} have carried out extensive calculations of CCF effects for $\text{Pr}^{3+}\text{-Cl}^-$ systems. Their calculations predict that the $\mathbf{G}_{10,A}^4$ parameters are important, and they obtain the same signs as we do from our fits. Analysis of their results shows that the major contribution to these parameters is excitations from lanthanide core states, such as $5p$ to $4f$, and we have checked this with a simple calculation.

Judd¹⁶ has proposed a simple δ -function interaction model for the CCF. This model predicts that only the $\mathbf{g}_1^{(K)}$, $\mathbf{g}_2'^{(K)}$, $\mathbf{g}_3^{(K)}$, and $\mathbf{g}_{10}^{(K)}$ operators will be nonzero. Though the physical significance of such a simple model is unclear, its prediction of the importance of the $\mathbf{g}_2'^{(K)}$ and $\mathbf{g}_3^{(K)}$ (i.e., SCCF) and the $\mathbf{g}_{10}^{(K)}$ operators considered here must be more than a coincidence.

II. THE ${}^2H_{11/2}$ MULTIPLETS OF Nd^{3+}

Faucher and co-workers⁶ have given a detailed discussion of the difficulty of fitting the crystal-field splitting of the ${}^2H_{11/2}$ multiplets of Nd^{3+} . There are two ${}^2H_{11/2}$ multiplets in the f^3 configuration, labeled ${}^2H(1)_{11/2}$ and ${}^2H(2)_{11/2}$ in the notation of Nielson and Koster.¹⁷ The multiplets are mixed by the Coulomb and spin-orbit interactions, so the multiplets observed in the ions contain the linear combinations given in Table I (we omit contributions from ${}^2I_{11/2}$ and ${}^4G_{11/2}$).

Reduced matrix elements of $\mathbf{C}^{(4)}$ and $\mathbf{g}_{10,A}^{(4)}$ are given in

TABLE I. Eigenvector components of the ${}^2H_{11/2}$ multiplets of Nd^{3+} . Parameter values are from Ref. 9.

Energy (cm^{-1})	${}^2H(1)_{11/2}$	${}^2H(2)_{11/2}$
15 783	-0.3558	0.8949
33 959	0.8220	0.3783

TABLE II. Pure $^{2S+1}L_J$ reduced matrix elements of the $C^{(4)}$ and $g_{10A}^{(4)}$ operators for the ${}^2H_{11/2}$ multiplets of Nd^{3+} .

	$C^{(4)}$	$g_{10A}^{(4)}$
$\langle {}^2H(1)_{11/2} {}^2H(1)_{11/2} \rangle$	-0.329	0
$\langle {}^2H(1)_{11/2} {}^2H(2)_{11/2} \rangle$	0.674	-0.109
$\langle {}^2H(2)_{11/2} {}^2H(2)_{11/2} \rangle$	0.537	0.568

Table II. These are the matrix elements obtained *before* taking into account mixing induced by the Coulomb and spin-orbit interactions. In Table III we give the matrix elements for several fourth-rank operators obtained after taking into account this mixing.

It is clear from Tables I–III that there is considerable cancellation in the reduced matrix element of $C^{(4)}$ for the ${}^2H(2)_{11/2}$ multiplet (Table III). This is discussed in detail by Faucher *et al.*⁶ (see their Fig. 2). The problem with the Nd^{3+} spectra is that the splitting calculated for the ${}^2H(2)_{11/2}$ multiplet is too small. Faucher *et al.* have made several suggestions for modifying the matrix elements to improve this situation. One suggestion was to “switch off” the off-diagonal matrix elements of $C^{(4)}$ between ${}^2H(1)_{11/2}$ and ${}^2H(2)_{11/2}$. Another was to divide the diagonal matrix element of $C^{(4)}$ for ${}^2H(2)_{11/2}$ by four (before allowing for mixing).⁷

Table II shows that the latter suggestion is approximately the same as introducing the operator $g_{10A}^{(4)}$, with parameter ratios $G_{10AQ}^{(4)}/B_Q^{(4)}$ around $-\frac{3}{4}$. Since $g_{10A}^{(4)}$ has rather small matrix elements for most of the other experimentally observed multiplets of Nd^{3+} the addition of $g_{10A}^{(4)}$ has little effect on the generally good fit for the rest of the spectrum.

Table III shows that the operators $g_2^{(4)}$ and $g_3^{(4)}$, and therefore the fourth-rank SCCF operator, have very small matrix elements within the ${}^2H(2)_{11/2}$ multiplet. [From now on when we refer to ${}^2H(2)_{11/2}$ we mean the multiplet which is *predominantly* ${}^2H(2)_{11/2}$ —see Table I.]. Therefore we can conclude straight away that the fourth-rank SCCF parameters will not be useful. The $g_3^{(6)}$ operator has larger matrix elements, but it did not prove effective in the data fits—the problem for the ${}^2H(2)_{11/2}$ multiplet seems to lie with the fourth-rank operators.

III. DATA FITS

To test the effectiveness of various CCF operators on the whole Nd^{3+} spectrum we have carried out extensive

TABLE IV. $Nd^{3+}:\text{LaCl}_3$ parameter fits with and without $G_{10A}^{(4)}$. All standard deviations and crystal-field parameters are in cm^{-1} . Errors are given in parentheses. Data are from Ref. 9. See text for definition of $G_{10A}^{(4)}$.

	LaCl_3 I	LaCl_3 II
n	87	87
σ	6.9	6.0
$\sigma({}^2H(2)_{11/2})$	10.1	4.2
B_0^2	181(7)	192(7)
B_0^4	-323(11)	-303(5)
B_0^6	-740(20)	-741(10)
B_6^6	464(10)	464(9)
G_{10A}^4		382(18)
G_{10A}^4/B_0^4		-0.93(0.07)

data fits on several crystal systems. Here we only report on those systems for which a large number of energy levels have been observed, so we consider a smaller number of systems than Faucher and co-workers.^{6,7} Our main conclusion is that only the operator $g_{10A}^{(4)}$ is consistently useful. For our largest data sets, $Nd^{3+}:\text{YAG}$ and $Nd^{3+}:\text{LaF}_3$, we have found some other operators helpful, and we feel that if some of the other data sets were extended, they too would benefit from these other operators.

The introduction of the CCF operators was treated as follows. First a fit was carried out using just the usual B_Q^k crystal-field parameters. The CCF parameters were then introduced, but the ratios of the various Q components were fixed in the same ratio as those found experimentally for the $B_Q^{(k)}$ parameters. The parameter $G_{10A}^{(4)}$ thus multiplies the operator

$$g_{10A}^{(4)} \equiv g_{10A0}^{(4)} + \sum_{Q \neq 0} g_{10AQ}^{(4)} (B_Q^4/B_0^4) \quad (5)$$

(which is different for each host crystal).

Some fits were done allowing the operators with different Q to vary independently. In most cases the ratios of the CCF parameters were similar to the ratios of the one-electron parameters, as we found in Ref. 2. However, in low-symmetry cases, such as LaF_3 , this is not always the case. It is not clear that the ratios should be *exactly* the same for the CF and CCF parameters, but if the superposition model is accurate it does seem reasonable, since the ratios are largely a *geometric* effect, i.e., they de-

TABLE III. Diagonal “free-ion” reduced matrix elements of selected operators for several multiplets of Nd^{3+} . These matrix elements take into account mixing by the Coulomb and spin-orbit interactions, using parameters taken from Ref. 9.

Multiplet energy (cm^{-1})	${}^2H(2)_{11/2}$ 15 783	${}^2H(1)_{11/2}$ 33 959	${}^2F(2)_{5/2}$ 38 078	${}^2F(2)_{7/2}$ 39 440
$C^{(4)}$	-0.029	0.108	-0.142	-0.189
$g_2^{(4)}$	0.002	-0.009	-0.086	-0.325
$g_3^{(4)}$	-0.061	0.243	0.058	-0.019
$g_{10A}^{(4)}$	0.518	0.009	0.256	0.179
$g_{10B}^{(4)}$	0.249	0.013	0.070	-0.063

TABLE V. NdODA ($\text{Na}_3[\text{Nd}(\text{C}_4\text{H}_4\text{O}_5)_3 \cdot 2\text{NaClO}_4]$) parameter fits with and without G_{10A}^4 . All standard deviations and crystal-field parameters are in cm^{-1} . Errors are given in parentheses. Data are from Ref. 13. See text for definition of G_{10A}^4 .

	ODA I	ODA II
n	114	114
σ	18.2	14.4
$\sigma(^2H(2)_{11/2})$	35.6	20.0
B_0^2	-26(21)	-16(16)
B_0^4	-1031(34)	-976(27)
B_3^4	-843(26)	-827(20)
B_0^6	-488(35)	-504(28)
B_3^6	-1029(29)	-1035(23)
B_6^6	-674(33)	-649(26)
G_{10A}^4		370(34)
G_{10A}^4/B_0^4		-0.38(0.05)

pend to a large extent on the *angular* coordinates of the ligands.^{1,2}

Our results are summarized in Tables IV–IX. In these tables n is the number of observed levels, σ the overall standard deviation, and $\sigma(^2H(2)_{11/2})$ the deviation for the $^2H(2)_{11/2}$ multiplet. Estimated errors for the fitted parameters are given in parentheses. The fitting method is the same as that used in our previous work.² The free-ion parameters are not shown in the tables. They were allowed to vary freely, and always took on values similar to those given in Refs. 9 and 11.

Note that the G_{10A}^4 parameters are well determined, according to the statistical tests of the data-fitting routines. Also, the values of the $B_Q^{(4)}$ parameters are not strongly affected by the addition of the $\mathbf{g}_{10A}^{(4)}$ operator, though there seems to be a tendency for the $B_Q^{(4)}$ to become slightly smaller. This reflects the fact that the $\mathbf{g}_{10A}^{(4)}$ operator has small matrix elements for most of the multiplets observed experimentally.

For YAG and LaF_3 (Tables VIII and IX) we had par-

TABLE VI. NdAlO_3 parameter fits with and without G_{10A}^4 . All standard deviations and crystal-field parameters are in cm^{-1} . Errors are given in parentheses. Data are from Ref. 12. See text for definition of G_{10A}^4 .

	NdAlO_3 I	NdAlO_3 II
n	116	116
σ	10.6	10.1
$\sigma(^2H(2)_{11/2})$	13.9	11.7
B_0^2	-469(12)	-463(11)
B_0^4	563(18)	547(18)
B_3^4	-419(15)	-418(15)
B_0^6	-1713(18)	-1708(17)
B_3^6	-960(17)	-974(16)
B_6^6	-1071(16)	-1067(15)
G_{10A}^4		-154(25)
G_{10A}^4/B_0^4		-0.28(0.05)

TABLE VII. $\text{Nd}^{3+}:\text{LiYF}_4$ parameter fits with and without G_{10A}^4 . All standard deviations and crystal-field parameters are in cm^{-1} . Errors are given in parentheses. Data are from Ref. 10. See text for definition of G_{10A}^4 .

	LiYF_4 I	LiYF_4 II
n	121	121
σ	22.5	14.7
$\sigma(^2H(2)_{11/2})$	46.8	7.7
B_0^2	410(23)	372(15)
B_0^4	-978(38)	-960(25)
B_3^4	-1243(30)	-1181(19)
B_0^6	6(35)	-46(23)
B_3^6	-1058(28)	-1043(19)
G_{10A}^4		750(27)
G_{10A}^4/B_0^4		-0.78(0.05)

ticularly large data sets (over 140 observed levels) and we were able to obtain well-determined values for the parameters G_{10B}^4 and G_2^4 , in addition to G_{10A}^4 . Improvements to the high-lying 2F multiplets are noted in Tables VIII and IX. Without these and other high-energy multiplets the G_{10B}^4 and G_2^4 parameters are not well determined.

Table X shows the improvement obtained for the $^2H(2)_{11/2}$ multiplet when the $\mathbf{g}_{10A}^{(4)}$ operator is included in the LaF_3 fit. The inclusion of the $\mathbf{g}_{10A}^{(4)}$ operator “expands” the multiplet, to give much better agreement with experiment. Similar results were obtained for the other host crystals.

The ratio of G_{10A}^4/B_0^4 varies between -0.28 and -0.93 , with an average of about -0.6 . Note that the $\mathbf{g}_i^{(K)}$ operators are normalized differently for $i=1$ ($\mathbf{g}_1^{(K)} \equiv \mathbf{U}^{(K)}$) and $i>1$. For a quantitative comparison we must multiply the B_Q^K (which multiplies $C_Q^{(K)}$ rather than $U_Q^{(K)}$) by $14 \times (12/77)^{1/2}$ (strictly this is only accurate for f^2).² With this correction the “true” ratio is about -0.1 , i.e., the CCF effect is the order of 10% of the one-electron crystal field. However, since the $\mathbf{g}_2^{(4)}$, $\mathbf{g}_{10A}^{(4)}$, and $\mathbf{g}_{10B}^{(4)}$ operators have large matrix elements chiefly in the high-energy, low-spin multiplets, the inclusion of the corresponding parameters have a relatively small effect on most observed levels.

Our parameter fits confirm the analyses of Faucher *et al.*,⁷ in that the matrix element modifications proposed by them for the $^2H_{11/2}$ multiplets are consistent with our parameters (see Sec. II). The advantage of our approach is that we have introduced the parameter G_{10A}^4 , which we can now compare with *ab initio* calculations, whereas their adjustment of matrix elements is somewhat arbitrary and is difficult to interpret physically. Even though we have emphasized the connection between our results and those of Faucher *et al.*,⁷ we should emphasize that our work proceeded independently and the comparison with their results was made *after* most of our data fits had been done.

IV. AB INITIO CALCULATIONS

Ng and Newman^{14,15} have carried out extensive *ab initio* calculations of CCF effects for the model system

TABLE VIII. $\text{Nd}^{3+}:\text{YAG}$ ($\text{Y}_3\text{Al}_5\text{O}_{12}$) parameter fits with and without G_{10A}^4 . All standard deviations and crystal-field parameters are in cm^{-1} . Errors are given in parentheses. Data are from Ref. 8. See text for definition of G_2^4 , G_{10A}^4 , and G_{10B}^4 .

	YAG I	YAG II	YAG III	YAG IV
n	144	144	144	144
σ	31.1	18.6	17.4	15.3
$\sigma(^2H(2)_{11/2})$	74.1	13.1	10.3	9.9
$\sigma(^2F(2)_{5/2})$	80.3	31.3	27.3	23.6
$\sigma(^2F(2)_{7/2})$	58.9	35.3	39.9	8.6
B_0^2	-404(30)	-362(18)	-380(17)	-386(15)
B_2^2	180(28)	172(16)	175(15)	172(14)
B_0^4	-2821(51)	-2706(31)	-2728(29)	-2769(26)
B_2^4	532(54)	504(32)	517(30)	534(26)
B_4^4	1239(46)	1193(28)	1243(26)	1270(24)
B_0^6	955(56)	958(33)	982(31)	973(28)
B_2^6	-390(52)	-323(31)	-329(30)	-332(26)
B_4^6	1610(41)	1607(25)	1607(23)	1611(20)
B_6^6	-281(49)	-192(30)	-222(28)	-230(24)
G_2^{4A}				-804(45)
G_{10A}^4		1521(41)	1409(39)	1291(35)
G_{10B}^4			584(46)	601(41)
G_2^{4A}/B_0^4				0.29(0.01)
G_{10A}^4/B_0^4		-0.56(0.02)	-0.52(0.02)	-0.47(0.02)
G_{10B}^4/B_0^4			-0.21(0.02)	-0.22(0.02)

$\text{Pr}^{3+}\text{-Cl}^-$. The accuracy of these calculations could not be easily tested, since most of the parameters they calculated had not been determined experimentally. This was a major motivation in undertaking the present work.

Ng and Newman's calculations suffered from some convergence difficulties. This made their calculation of

the SCCF parameters somewhat uncertain (see Table XIII of Ref. 15). Fortunately these difficulties do not seem to apply to the parameters of interest in this paper.

If we examine Table XIV of Ref. 15 we see that G_{10A}^4 is quite prominent. In fact the ratios predicted for G_2^{4A}/B_0^4 , G_{10A}^4/B_0^4 , and G_{10B}^4/B_0^4 are 0.29, -0.50, and

TABLE IX. $\text{Nd}^{3+}:\text{LaF}_3$ parameter fits with and without G_{10A}^4 . All standard deviations and crystal-field parameters are in cm^{-1} . Errors are given in parentheses. Data are from Ref. 11. See text for definition of G_{10A}^4 .

	LaF ₃ I	LaF ₃ II	LaF ₃ III	LaF ₃ IV
n	146	146	146	146
σ	13.6	11.9	11.5	10.9
$\sigma(^2H(2)_{11/2})$	17.5	4.2	3.0	5.0
$\sigma(^2F(2)_{5/2})$	25.1	10.9	10.1	7.3
$\sigma(^2F(2)_{7/2})$	25.8	14.3	17.7	5.1
B_0^2	171(15)	175(12)	187(11)	188(11)
B_2^2	-138(14)	-122(12)	-122(12)	-123(11)
B_0^4	1183(22)	1139(19)	1179(19)	1218(18)
B_2^4	-69(27)	-73(23)	-66(23)	-75(22)
B_4^4	-11(22)	6(24)	3(23)	-5(21)
B_0^6	1434(22)	1417(19)	1410(19)	1401(18)
B_2^6	230(30)	241(25)	237(24)	246(23)
B_4^6	-205(23)	-214(20)	-220(19)	-230(18)
B_6^6	806(18)	814(16)	815(16)	814(16)
G_2^{4A}				544(40)
G_{10A}^4		-591(29)	-500(29)	-436(31)
G_{10B}^4			-281(33)	-325(32)
G_2^{4A}/B_0^4				0.45(0.04)
G_{10A}^4/B_0^4		-0.52(0.03)	-0.42(0.03)	-0.36(0.03)
G_{10B}^4/B_0^4			-0.24(0.03)	-0.27(0.03)

TABLE X. Energy levels for the ${}^2H(2)_{11/2}$ multiplet for LaF_3 (cm^{-1}). The parameters for LaF_3 I and LaF_3 II are given in Table IX.

Observed	LaF_3 I (No G_{10A}^4)		LaF_3 II (with G_{10A}^4)	
	Calc.	Difference	Calc.	Difference
15997	16025	-28	16006	-9
16033	16042	-9	16036	-3
16046	16049	-3	16047	-1
16060	16065	-5	16066	-6
16100	16093	7	16096	4
16165	16135	30	16165	0
σ		17.5		4.2

-0.15, which are very similar to our experimental results for YAG and LaF_3 (Tables VIII and IX).

It would be interesting to be able to determine the most important physical contributions to the correlation effects. By analyzing Ng and Newman's calculated results for contributions from various diagrams, we deduce that the largest contribution to the G_{10A}^4 parameter seems to come from excitations from the lanthanide core to the $4f$ orbitals.

As a rough check, we can use the formalism of Morrison *et al.*,¹⁸ along with estimates of radial integrals from Newman (Ref. 19, Sec. 5). Considering just excitations from $5p$ to $4f$, which would be expected to dominate, we obtain a positive value for G_2^4 , and negative values for G_{10A}^4 and G_{10B}^4 in the ratio 1:-2.3:-2.0.

V. JUDD'S δ -FUNCTION OPERATOR

Judd¹⁶ has investigated the possibility of modeling the CCF using a δ -function interaction with the ligands. The interaction has the form

$$I = \delta(\mathbf{r}_i - \mathbf{R}_L) \delta(\mathbf{r}_j - \mathbf{R}_L), \quad (6)$$

where \mathbf{r}_i and \mathbf{r}_j are coordinates of f electrons i and j , and \mathbf{R}_L is the coordinates of the ligand. An interesting fact about this operator is that when it is decomposed into $\mathbf{g}_i^{(k)}$ operators only $\mathbf{g}_1^{(K)}$, $\mathbf{g}_2^{(K)}$, $\mathbf{g}_3^{(K)}$, and $\mathbf{g}_{10}^{(K)}$ appear.¹⁶ We find that with Judd's model G_2^4 , G_3^4 , G_{10A}^4 , and G_{10B}^4 are predicted to have the ratios 1:-0.9:-0.5:-0.9. Although the physical interpretation of operator (6) is unclear, the correlation between the signs predicted by this model, our empirical results, and the *ab initio* calculations, is striking.

VI. OTHER IONS

Our previous calculations² for $\text{Gd}^{3+}:\text{LaCl}_3$ showed that, as well as the rank-6 SCCF, some fourth-rank CCF operators could be important. G_{10A}^4 was one of the possible operators. The ratio of G_{10A}^4/B_0^4 in the fit reported in

Table X of Ref. 2 is -0.27. However, it should be noted that \mathbf{g}_{10A}^4 was *not* the most effective rank-4 operator for that system.

The 1D_2 multiplet of Pr^{3+} is another multiplet that is often difficult to fit using the one-electron crystal-field parametrization. The reduced matrix elements of $\mathbf{C}^{(4)}$, $\mathbf{g}_{10A}^{(4)}$, and $\mathbf{g}_{10B}^{(4)}$ for this multiplet are 0.646, 0.391, and -0.454. G_{10A}^4 and G_{10B}^4 could therefore have a large effect on this multiplet, but if both parameters have the same sign and roughly the same magnitude, as they do in our $\text{Nd}^{3+}:\text{YAG}$ and $\text{Nd}^{3+}:\text{LaF}_3$ fits, then the effects of the two operators will tend to cancel out. Thus, it is difficult to be conclusive. Interestingly, the "orbitally correlated crystal field" (LCCF) proposed by Yeung and Newman²⁰ to improve the fit for this ion does *not* include the $\mathbf{g}_{10}^{(K)}$ operators.²

The ${}^2H(2)_{11/2}$ multiplet of Er^{3+} , like its counterpart in Nd^{3+} , tends to have its splitting underestimated by the one-electron crystal-field model. Preliminary fits yield similar ratios for G_{10A}^4/B_0^4 in Er^{3+} systems as determined in this paper for Nd^{3+} . It should be noted that the matrix elements of $\mathbf{C}^{(4)}$, but not the CCF operators, change sign relative to those for Nd^{3+} .

VII. CONCLUSIONS

We have confirmed that the examination of anomalous multiplets is a useful approach to determining CCF parameters. We emphasize that in this study we tried all possible CCF operators. Only those which gave a significant effect are reported. The $\mathbf{g}_3^{(K)}$ operators (i.e., the SCCF) are not very useful for Nd^{3+} , but on the other hand the $\mathbf{g}_{10A}^{(4)}$ operator was not found to be useful for Ho^{3+} . There are many CCF operators and a careful study of all the lanthanide ions will probably be necessary to determine their values.

It would be a large task to exhaust the possibilities of the lanthanide and actinide spectra currently available in the literature. At the same time more effort should be made to extend the measurements to higher energies. We have noted that more information was available from the $\text{Nd}^{3+}:\text{YAG}$ and $\text{Nd}^{3+}:\text{LaF}_3$ spectra, because high-energy multiplets were included. Larger data sets would probably have yielded values for G_{10B}^4 and G_2^4 for the other crystals. Correlation effects are likely to be most dramatic in the high-energy, low-spin-multiplicity multiplets, and techniques to extend the range of experimental data, for example, by using synchrotron radiation or two-photon absorption, will no doubt be very helpful in extending the data sets. Our sometimes dramatic improvements in the fits to certain high-energy multiplets suggests that the assignment of these energy levels may be hindered when only the one-electron crystal field is considered.

It is pleasing that the parameters obtained here bear some relation to *ab initio* calculations, since it is the long-term aim of studies such as this to understand the physical origin of the correlation effects. The ${}^2H(2)_{11/2}$ multiplet of Nd^{3+} which we have concentrated on in this paper appears to be strongly affected by $5p \rightarrow 4f$ excita-

tions, though we can only consider this a tentative conclusion at this point. In seeking more clues about correlation-crystal-field effects we suspect that group-theoretical analyses, such as that of Judd's δ -function operator, will be useful.

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- ¹D. J. Newman and B. Ng, *Rep. Prog. Phys.* **52**, 699 (1989).
²M. F. Reid, *J. Chem. Phys.* **87**, 2875 (1987).
³B. R. Judd, *J. Chem. Phys.* **66**, 3163 (1977).
⁴H. Crosswhite and D. J. Newman, *J. Chem. Phys.* **81**, 4959 (1984).
⁵B. R. Judd, *Phys. Rev. Lett.* **39**, 242 (1977).
⁶M. Faucher, D. Garcia, P. Caro, J. Derouet, and P. Porcher, *J. Phys. (Paris)* **50**, 219 (1989).
⁷M. Faucher, D. Garcia, and P. Porcher, *C. R. Acad. Sci. Ser. II* **308**, 603 (1989).
⁸M. F. Reid, C. L. Li, C. K. Jayasankar, and F. S. Richardson (unpublished).
⁹H. M. Crosswhite, H. Crosswhite, F. W. Kaseta, and R. Sarup, *J. Chem. Phys.* **64**, 1981 (1976).
¹⁰A. A. S. Da Gama, G. F. de Sa, P. Porcher, and P. Caro, *J. Chem. Phys.* **75**, 2583 (1981).
¹¹W. T. Carnall, G. L. Goodman, K. Rajnak, and R. S. Rana, *J. Chem. Phys.* **90**, 3443 (1989).
¹²E. Antic-Fidancev, M. Lemaitre-Blaise, L. Beaury, B. Teste de Sagey, and P. Caro, *J. Chem. Phys.* **73**, 4613 (1980).
¹³P. S. May, C. K. Jayasankar, and F. S. Richardson, *Chem. Phys.* **138**, 115 (1989).
¹⁴B. Ng and D. J. Newman, *J. Chem. Phys.* **87**, 7096 (1987).
¹⁵B. Ng and D. J. Newman, *J. Chem. Phys.* **87**, 7110 (1987).
¹⁶B. R. Judd, in *Group Theoretical Methods in Physics*, Vol. 79 of *Lecture Notes in Physics*, edited by P. Kramer and A. Rieckers (Springer-Verlag, Berlin, 1978), p. 417.
¹⁷C. W. Nielson and G. F. Koster, *Spectroscopic Coefficient for the p^N , d^N , and f^N Configurations* (MIT Press, Cambridge, Mass., 1963).
¹⁸J. C. Morrison, P. R. Fields, and W. T. Carnall, *Phys. Rev. B* **2**, 3526 (1970).
¹⁹D. J. Newman, *J. Phys. C* **10**, 4753 (1977).
²⁰Y. Y. Yeung and D. J. Newman, *J. Chem. Phys.* **86**, 6717 (1987).