TERM DEPENDENT CORRELATION CRYSTAL FIELD TO THE $^2H(2)_{11/2}$ LEVELS OF Nd^{+3}:$LiYF_4$

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Abstract. Phenomenological crystal field parameters reproduces quite satisfactorily the splittings of a very large number of levels to Nd^{3+}:$LiYF_4$ but give less than half the observed splitting of the $^2H(2)_{11/2}$ multiplet. Phenomenological two-body crystal field parameters were able to account for more than 50% of this discrepancy.

Crystal-field theory has succeded in foreseing the splittings of the rareearth $4f^N$ multiplet levels in crystals. Phenomenological crystal field parameters obtained by fitting a small number of crystal field levels of the ion in a particular host reproduce quite well the splittings of the other multiplest at the same host[1]. Ab initio calculations using the point charge electrostatic model (P.C.E.M.), give large discrepancies between theoretical and experimental crystal field levels[2]. Recently a simple overlap model[3] was able to rectify part of these discrepancies.

Judd suggested that this discrepancy could be partially rectified by considering the term dependent correlation crystal field[4].

In the present work we propose to examine how two-body crystal field operators, required to correct the Pr^{3+} spectra in a particular host, could be used to explain the discrepancies in the Nd^{3+} spectra in the same host. This analysis is simplified because the two-body coefficients of fractional parentage between electronic configuration $4f^3$ and $4f^2$ are easily related to one-body coefficients.

When configuration interaction is considered is crystal field theory, two-body operators may appear which should be included in the Hamiltonian[5]. The two-body Hamiltonian of the correlation crystal field can be conveniently writen as[4].

$$H_{CCF} = \sum_{\substack{k,q \\ k_1,k_2}} B_{KQ}(k_1,k_2)\, X_Q^{(k)}(k_1,k_2) \tag{1}$$

where k_1, k_2 are associated with one-body operators and are subjected to the condition $k_1, k_2 \leq 6$ K is an even number. Whose maximum value is 12.

The matrix elements of the operators in (1) for the coupled $|4f^N \alpha SLJM\rangle$ states show the same 3j and 6j simbols related to the coupling of L-S states and to one-body operators. For $4f^2$ the matrix elements on the L-S basis can be easily calculated. The result is

$$\langle n\ell^2 SLM_S M_L | X_Q^{(k)}(k_1,k_2) | n\ell^2 S'L'M'_S M'_L\rangle$$

$$= (-1)^{L-M_L} \begin{pmatrix} L & K & L' \\ -M_L & Q & M'_L \end{pmatrix} [(2L+1)(2L'+1)(2K+1)]^{1/2} \begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k_2 \\ L & L' & K \end{Bmatrix} \langle \ell||k_1||\ell\rangle\langle \ell||k_2||\ell\rangle\, \delta_{SS'}\, \delta_{M_S M'_S} \tag{2}$$

Since the matrix elements for $4f^N$ can be obtained from those of $4f^2$, using fractional parentage coefficients, it is covenient to define correlation crystal field parameters for $4f^2$ as[4]

$$B_{KQ}(L,L') = \sum_{k_1,k_2} B_{KQ}(k_1,k_2)\langle 4f^2SL||X^{(k)}(k_1,k_2)||4f^2SL'\rangle \tag{3}$$

For the $4f^3$ configuration the calculation can be simplified using second quantization techniques.

The second quantization form of the two-body operator is

$$X_Q^{(K)} = \frac{1}{2} \sum_{\substack{m_1 m_2 \\ m'_1 m'_2}} a^+_{m_1} a^+_{m_2} \langle m_1 m_2 | X_Q^{(K)} | m'_1 m'_2\rangle a_{m'_2} a_{m'_1} \tag{4}$$

and with the coupled $m_1 m_2$ states we may write

$$X_Q^{(K)} = \sum_{\substack{LM \\ L'M'}} (a^+a^+)^L_M \langle LM | X_Q^{(K)} | L'M'\rangle (aa)^{L'}_{M'} \tag{5}$$

Now using the Wigner-Eckart theorem we may write

$$X_Q^{(K)} = \sum_{\substack{LM \\ L'M'}} (a^+a^+)^L_M \langle LML'M'|KQ\rangle\langle L||X^{(K)}||L'\rangle (aa)^{L'}_{M'} \tag{6}$$

and then coupling the creation and annihilation operators

$$X_Q^{(K)} = \sum_{LL'} \{(a^+a^+)^L (aa)^{L'}\}^K_Q \langle L||X^{(K)}||L'\rangle \tag{7}$$

Now the correlation crystal field parameter for $4f^3$ can be defined as related a term dependent parameter of $4f^2$[4]

$$B_{KQ}(4f^3;\, \alpha L, \alpha' L') = B_{KQ}(\bar{L},\bar{L}')\langle 4f^3 \sigma SL||\{(a^+a^+)^{\bar{L}}(aa)^{\bar{L}'}\}^K||4f^3\alpha' SL'\rangle \tag{8}$$

The reduced matrix elements of eq.(9) can be calculated as a particular case of a double tensor, scalar in spin space, of eq.(34) in ref. [6].

$$\langle 4f^3\alpha SL||\{(a^+a^+)^{0\bar{L}}(aa)^{0\bar{L}'}\}^{0K}||4f^3\alpha' SL'\rangle = (2K+1)^{1/2}(-1)^{2S+K} \begin{pmatrix} 0 & 0 & 0 \\ S & s & S \end{pmatrix} \begin{pmatrix} \bar{L} & K & \bar{L}' \\ L & \ell & L' \end{pmatrix} \cdot \langle 4f^3\alpha SL||(a^+a^+)^{0\bar{L}}||4f's\ell\rangle\langle 4f's\ell||(aa)^{0\bar{L}'}||4f^3\alpha' SL'\rangle \tag{9}$$

For $4f^3$ the two-body creation an annihilation matrix elements can be easily calculated if we use the equation

$$\langle 4f^3\alpha SLM_SM_L|(a^+a^+)^{0\bar{L}}_{0M_L}|4f's\ell m_s m_\ell\rangle =$$

$$= (-1)^{L-M_L+S-M_S}\begin{pmatrix} L & L & \ell \\ -M_L & M_L & m_\ell \end{pmatrix}\begin{pmatrix} S & 0 & s \\ -M_S & 0 & m_s \end{pmatrix} . \qquad (10)$$

$$\langle 4f^3\alpha SL||(a^+a^+)^{0\bar{L}}||4f's\ell\rangle$$

Writing one particle state in second quantization form, the creation operators can be comuted to give

$$\langle 4f^3\alpha SLM_SM_L|a^{+1/23}_{m_s m_\ell}(a^+a^+)^{0\bar{L}}_{0M_L}|0\rangle$$

$$= \sqrt{2}(-1)^{L-M_L+S-M_S}\begin{pmatrix} L & \ell & \bar{L} \\ -M & m_\ell & M_L \end{pmatrix}\begin{pmatrix} S & s & 0 \\ -M_S & m_s & 0 \end{pmatrix} . \qquad (11)$$

$$\langle 4f^3\ SL||a^+||4f^2 0\bar{L}\rangle$$

from (10) and (11) we may that

$$\langle 4f^3\ SL||(a^+a^+)^{0\bar{L}}||4f's\ell\rangle = \qquad (12)$$

$$= (-1)^{S+s+L+\bar{L}+\ell}\sqrt{2}\langle 4f^3\alpha SL||a^+||4f^2 0\bar{L}\rangle$$

The one particle matrix element is related to parentage coeficient[6] through

$$\langle 4f^3\alpha SL||a^+||4f^2 0\bar{L}\rangle = \qquad (13)$$

$$= (-1)^3\{(2S+1)(2L+1)\}^{1/2}\langle 4f^3\alpha SL\{|4f^2 0\bar{L}\rangle$$

with a phase facot $(-1)^{\bar{S}+\bar{L}-s-S-\ell-L}$ for the complex conjugated of eq. [13].

Now the matrix elements of Eq.(8) can be writen as

$$\langle 4f^3\alpha SL||\{(a^+a^+)^{0\bar{L}}(aa)^{0\bar{L}}\}^{0K}||4f^3\alpha' SL\rangle =$$

$$= (2K+1)^{1/2}(-1)^K\begin{pmatrix} 0 & 0 & 0 \\ S & s & S \end{pmatrix}\begin{Bmatrix} \bar{L} & K & \bar{L} \\ L & \ell & L \end{Bmatrix} 6(2S+1)(2L+1)$$

$$\langle 4f^3\alpha SL\{|4f^2 0\bar{L}\rangle\langle 4f^3\alpha' SL\{|4f^2 0\bar{L}\rangle \qquad (14)$$

with $x = S + K + \bar{S} + \bar{L} - s - \ell - L$.

The contributions with $\bar{L} \neq \bar{L}'$ and $L \neq L$ were neglected since they are necessary only in case of very large mixture of terms[4].

The $^2H(2)$ levels of $4f^3$ have parentage with the ^1D, ^1G and ^1K levels of $4f^2$. From eq. (14) can be easily calculated a term dependent correlation crystal field coefficient for B_{KQ} $(\bar{L})$ parameter of $4f^2$ to give $B_{KQ}(\alpha,\alpha';L)$ of $4f^3$. The matrix elements of eq.(14) for $^2H(2)$ are very small for $K \geq 8$. With ^1D $(\bar{L}=2)$ there are contribution for $K=2,4$ and with ^1G $(\bar{L}=4)$ for $K = 2, 4, 6$.

The wave function of the ^1D levels of $4f^2$ is more than 90% free of mixture with the other levels. For these levels in $LiYF_4$, the crystal field parameters need to be changed by 87 cm^{-1} for B_{20}, 280 cm^{-1} for B_{40} and 150 cm^{-1} for B_{44}. If these quantities can be taken as the correlation crystal field for the ^1D levels of Pr^{3+} in $LiYF_4$, the matrix elements of eq.(14) between the $^2H(2)$ or $^2H(1)$ and the ^1D levels gives the parameters for the $^2H(2)_{11/2}$ levels of Nd^{3+} in the same host. Table 1 shows the crystal field parameters that reproduces the splittings of all levels and the term dependent correlation crystal field parameter for the ^2H levels.

TABLE 1 - Crystal field parameters for Nd^{3+} in $LiYF_4$ (cm^{-1})

	all levels	$^2H(2)$	$^2H(2)/^2H(1)$	$^2H(1)$
B_{20}	401	816	609	487
B_{40}	-1008	-431	-720	-888
B_{44}	-1230	-921	-1075	-1165
B_{60}	30	30	30	30
B_{66}	-1075	-1075	-1075	-1075

The splitting of the $^2H(2)_{11/2}$ multiplet increases by more than 50% after the correlation crystal field is included (table 2). This gives some confidence to the hypothesis that two-body correlation effects may be of great importance in crystal-field theory because there is no fitting to the experimental results of Nd^{3+} terms that come from Pr^{3+} terms of difficult description by the one-body crystal field operator. In this work a truncated matrix for $4f^3$ was used containin only the twelve components of the ^2H levels. A more complete calculation, using a non truncated basis is in progress.

TABLE 2 - Energy level splittings of $^2H(2)_{11/2}$ in cm^{-1}

level	Exp.[1]	Cal.[1]	(a)	(b)
±11/12	123	60	32	66
±1/2	42	32	31	53
±5/2	-	3	-1	-1
±9/2	-22	-10	-2	-12
±7/2	-48	-29	-22	-44
±3/2	-94	-31	-42	-66

(a) Calculated with truncated $^2H(2)_{11/2}$, $^2H(1)_{11/2}$ matrix and parameters of ref.1. (b) Calculated with truncated $^2H(2)_{11/2}$, $^2H(1)_{11/2}$ matrix and parameters modified by correlation crystal field contribution.

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