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LETTER TO THE EDITOR

Parameters of the correlated crystal field for trivalent holmium in YVO_4 , YAsO_4 and HoPO_4

B Pilawa

Physikalisches Institut, Universität Karlsruhe (TH), PO Box 6980, D-7500 Karlsruhe 1,
Federal Republic of Germany

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Abstract. A parametric description of the crystal-field splittings of Ho^{3+} in the three host lattices YVO_4 , YAsO_4 and HoPO_4 is given in the energy range from 0 to $\sim 28000 \text{ cm}^{-1}$. The influence of electron correlation is taken into consideration by five additional parameters. The crystal-field Hamiltonian was diagonalized using a basis including all terms up to 35000 cm^{-1} (316 states). Differences between the experimentally obtained crystal-field components and the calculated ones are usually smaller than 4 cm^{-1} .

The J -terms of a Ho^{3+} ion substituted into a host lattice are split by the crystal-field interaction into a number of components. The energies of these crystal-field components are normally calculated using a phenomenological crystal-field Hamiltonian which does not take electron correlation into account. These calculations are more or less satisfactory in a wide energy range (0 to 21000 cm^{-1}). At higher energies differences occur between the experimentally determined crystal-field components and the theoretically predicted ones which are especially large for Ho^{3+} in the host lattices of YVO_4 , YAsO_4 and HoPO_4 . These differences might be the result of experimental difficulties. It seems *more likely however that they are caused by contributions that are not included in the simple crystal-field Hamiltonian*; the most important of these will be the influence of electron correlation. Doubts on the reliability of the experimentally determined crystal-field components prompted Enderle *et al* (1990a, b, c) to re-examine the absorption spectra of Ho^{3+} in these three host lattices. They extended the experimental work and showed that the differences between experiment and theory are not caused by experimental uncertainties. Hence, electron correlation must be the main reason for the differences.

The way to include electron correlation into a phenomenological crystal-field description was pointed out by Bishton and Newman (1970). They introduced the correlated crystal field (CCF). Since it is very difficult to ascertain the strength of the CCF and the values of the related parameters by an *ab-initio* calculation (Ng and Newman 1987), we used experimental results for Ho^{3+} in host lattices with zircon structure to determine the influence of the CCF by a comparison between experiment and theory. An investigation by Pilawa (1991a, henceforth to be referred to as paper I) led to the following results. The most significant influence on the crystal-field splittings is caused by the crystal-field operators of rank 4. It could be shown that three CCF operators had to be retained in order to get an adequate description of the observed splittings. To

consider the electron correlation connected with operators of rank 2, only one CCF operator had to be introduced. The correlation effects involved by operators of rank 6 could already be described by the spin-correlated crystal field (SCCF) which was introduced by Judd (1977) to reduce the number of operators in comparison with the CCF.

These results are of more general validity for the spectra of Ho^{3+} as was confirmed by an investigation of the crystal-field splittings of Ho^{3+} substituted into the hexagonal host lattices of LaCl_3 and $\text{Y}(\text{OH})_3$ (Pilawa 1991b).

In determining the CCF operators, which are most important for a parametrization of the splittings of Ho^{3+} , in the previous investigations it was necessary to simplify the crystal-field calculation. First of all, J -mixing was ignored. Only those terms whose splittings were assumed to be affected by J -mixing to a minor extent were considered. Instead of considering the crystal-field components of all terms at once, 'term-dependent' crystal-field parameters were determined for each individual term. By means of the reduced matrix elements of the CCF and SCCF operators it was possible to obtain 'term-independent' parameters. In the course of these calculations it turned out that only a small number of correlated crystal-field operators are necessary to describe electron correlation observed within the investigated spectral range (paper I). There are, however, two disadvantages of calculating 'term-independent' parameters in this way. Firstly, the influence of J -mixing on the crystal-field splittings is neglected completely and secondly, a direct comparison between the experimentally observed crystal-field splittings and those predicted by means of the obtained 'term-independent' parameters, in order to further refine the parameters, is not possible.

Now, we have extended the calculations to control whether or not there are significant influences of the simplifications on the values of the crystal-field parameters. Hence J -mixing was included by diagonalizing the whole crystal-field Hamiltonian and the detour via 'term-dependent' parameters was omitted. Thus a direct comparison between experiment and theory could be carried out. For the theoretical description of the measured crystal-field splittings, the following crystal-field operator was used:

$$H_{\text{CF}} = \sum_{k=2,4,6} \sum_{q=0,\pm 4} e_{q,1}^{(k)} \left(O_{q,1}^{(k)} + \sum_{\substack{t \\ t \neq 1}} c_{q,t}^{(k)} * O_{q,t}^{(k)} \right).$$

H_{CF} is invariant under the symmetry transformations of the site symmetry $\bar{4}2m$ of Ho^{3+} in the zircon structure compounds. Consequently the $e_{q,1}^{(k)}$ are real and $e_{q,1}^{(k)} = e_{-q,1}^{(k)}$ holds. The $O_{q,1}^{(k)}$ are one-electron operators which are proportional to the tensor operators $\Sigma_t^{(k)}(i)$ (where i is the electron on which the operator acts). $O_{q,t}^{(k)}$ ($t \neq 1$) are linear combinations of $\Sigma_t^{(k)}(i)$ with CCF or SCCF operators and $c_{q,t}^{(k)} = e_{q,t}^{(k)}/e_{q,1}^{(k)}$. As was found in Pilawa 1991b the ratios $c_{q,t}^{(k)}$ do not depend on the q values. For the following calculations it was presumed that the dominant contributions are produced by the operators that were found to lead to the most important contributions using the calculations described in paper I. Thus five parameters $c_{q,t}^{(k)}$ were used to take the electron correlation into consideration. The operators $O_{q,t}^{(k)}$ are presented in table 5 of paper I. In order to include J -mixing the matrix elements of H_{CF} were calculated between all crystal-field components up to $35\,000\text{ cm}^{-1}$ (316 states, apportioned into the five symmetry types of $\bar{4}2m$). So the diagonalization of the crystal-field matrix takes into account the influence of J -mixing, which is not only induced by the terms which were observed in experiment but also by terms that are lying at higher energies. The atomic parameters necessary to calculate the intermediate wavefunctions were the same as used and given in paper I.

Table 1. Crystal-field parameters. Columns (a): without inclusion of electron correlation; columns (b): electron correlation included. All figures have the units cm^{-1} .

	YVO ₄		YAsO ₄		HoPO ₄	
	(a)	(b)	(a)	(b)	(a)	(b)
$e_{0,1}^{(2)}$	134	164	28	63	-284	-235
$e_{0,1}^{(4)}$	362	428	52	7	54	46
$e_{4,1}^{(4)}$	-743	-895	-691	-780	-689	-743
$e_{0,1}^{(6)}$	778	834	720	751	807	833
$e_{4,1}^{(6)}$	-107	-135	41	83	44	65
$c_{3,3}^{(2)}$	—	-0.10	—	-0.73	—	0.40
$c_{3,3}^{(4)}$	—	-0.15	—	-0.11	—	-0.12
$c_{3,3}^{(4)}$	—	0.19	—	0.24	—	0.26
$c_{3,3}^{(4)}$	—	0.19	—	0.21	—	0.24
$c_{3,3}^{(6)}$	—	-0.14	—	-0.10	—	-0.10

Two different fitting procedures were carried out to find the crystal-field parameters for Ho^{3+} in YVO_4 , YAsO_4 and HoPO_4 . The first procedure was restricted to the terms of the multiplets 5I_7 and 5F for which it is known that the crystal-field operator without inclusion of electron correlation yields very good results. Thus no CCF and SCCF operators were used ($c_{q,i}^{(k)} = 0$). In a second fit the CCF and SCCF operators were included and all observed crystal-field components were regarded. The parameter values obtained in the two fitting procedures are summarized in table 1. Additionally, this table includes the parameters $e_{0,1}^{(4)}$ and $e_{4,1}^{(6)}$, which, in most cases, are relatively small and therefore could not be determined in paper I. As a consequence of the introduction of orthogonal operators $O_{q,i}^{(k)}$ (see paper I) the parameter values $e_{q,1}^{(k)}$ are not very different for the two fits. They are in good agreement with the values obtained in paper I. This is also true for the ratios $e_{q,i}^{(k)}/e_{q,1}^{(k)} = c_{q,i}^{(k)}$. This shows that the inclusion of J -mixing within an extended crystal-field matrix does not change the values of the parameters significantly.

Table 2 gives the root mean square (RMS) deviations between the measured and calculated crystal-field components for each individual term indicating the extent of agreement between experiment and theory. The introduction of correlated crystal-field operators drastically reduces the RMS deviation of the terms $^3K_{8,7}$ and $^5G_{6,5,4}$ and additionally it improves the fit of the terms 3H_5 and 5G_2 . These two terms were not included when the correlated operators were selected in paper I. The fact that the fitting procedure of column (b) gives no improvement for 3H_5 of Ho^{3+} in YVO_4 , contrary to that for the other two compounds, indicates that a successful calculation of this term is only possible if the crystal-field components of the neighbouring 3H_6 are known. For the terms 5S_2 , $^5F_{2,1}$ and 3H_6 the agreement is not yet satisfactory. It is to be expected that further refinements will be achieved if more accurate atomic intermediate wavefunctions of the free Ho^{3+} ion will be used and additional CCF operators will be included. The refinement of the free-ion wavefunctions might be important for the terms 5S_2 , $^5F_{2,1}$ since the splittings of the neighbouring terms are satisfactorily described by the obtained CCF operators. The term 3H_6 on the other hand is the first one which seems to call for the inclusion of further CCF operators. Their influence might even grow with increasing

† The crystal-field components of the terms $^5I_{7,6,5}$ were recently determined by Bischof (1991).

Table 2. RMS deviations between the observed and calculated crystal-field components. Columns (a): without inclusion of electron correlation; columns (b): electron correlation included. All figures have the units cm^{-1} .

	YVO ₄		YAsO ₄		HoPO ₄	
	(a)	(b)	(a)	(b)	(a)	(b)
⁵ I ₇	5.4	5.0	3.2	4.1	1.6	1.7
⁵ I ₆	2.0	3.8	1.3	3.8	0.5	2.1
⁵ I ₅	1.9	4.9	2.3	4.4	2.8	2.3
⁵ F ₅	1.2	2.5	0.6	2.7	2.1	1.9
⁵ S ₂	3.4	3.8	2.9	2.9	3.1	3.3
⁵ F ₄	1.8	1.0	1.7	2.1	1.7	2.0
⁵ F ₃	1.0	1.1	0.8	1.8	1.7	1.6
⁵ F ₂	1.1	3.0	3.7	5.5	4.3	6.6
³ K ₈	7.7	2.0	6.5	1.8	9.1	3.1
⁵ G ₆	22.2	3.5	16.3	3.9	16.9	4.2
⁵ F ₁	9.7	8.4	0.3	1.6	16.9	14.3
⁵ G ₅	30.0	2.7	27.0	2.7	24.4	2.9
⁵ G ₄	9.4	3.5	9.7	2.8	9.9	3.5
³ K ₇	9.0	2.9	8.7	1.2	10.2	3.0
³ H ₅	12.0	14.3	13.2	5.8	11.3	2.4
³ H ₆	—	—	14.5	15.6	17.5	11.0
⁵ G ₂	—	—	—	—	16.6	3.4

energy. Thus an extension of the experimental investigation to higher energies would be highly desirable.

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