# Near-infrared crystal-field spectra of trivalent holmium in $HoVO_4$, $HoAsO_4$, $HoPO_4$ and $Y(OH)_3$

# Near-infrared crystal-field spectra of trivalent holmium in HoVO$_4$, HoAsO$_4$, HoPO$_4$ and Y(OH)$_3$

B Pilawa, S Müller and H G Kahle

Physikalisches Institut, Universität Karlsruhe (TH), POB 6980, D-76128 Karlsruhe, Federal Republic of Germany

**Abstract.** The polarized absorption spectra of Ho$^{3+}$ in HoVO$_4$, HoAsO$_4$, HoPO$_4$ and (Ho$_{0.1}$, Y$_{0.9}$)(OH)$_3$ were studied in the range from 11 000 to 13 500 cm$^{-1}$ at temperatures between 1.4 and 70 K in magnetic fields up to 4 T. The crystal-field splittings of the term $^5I_4$ were determined for the first time. Previous studies of the term $^5I_5$ were re-examined and completed. The experimental results were critically compared with crystal-field calculations.

## 1. Introduction

An attempt to fit the measured crystal-field splittings of the Ho$^{3+}$ ion using a single set of crystal-field parameters (according to a one-electron operator) leads to a very unsatisfactory agreement, especially for energies above 20 000 cm$^{-1}$. On the other hand, fitting the splittings of the individual terms separately produces term-dependent crystal-field parameters with large variations in the region of higher energies. The reason is that the crystal field acts, via electron correlation, dissimilarly on the different Russell–Saunders multiplets, with the consequence that the determined crystal-field parameters depend on the manner in which the term is composed of different Russell–Saunders multiplets (Rajnak and Wybourne 1964, Rajnak and Krupke 1967). At lower energies the Russell–Saunders approximation is a rather good one and the crystal-field parameters turn out to be almost equal for different terms.

In an earlier investigation we determined the crystal-field splittings of nearly all the terms, up to 27 600 cm$^{-1}$, of Ho$^{3+}$ in HoVO$_4$, HoAsO$_4$, HoPO$_4$ and (Ho$_{0.1}$, Y$_{0.9}$)(OH)$_3$ (Bischoff *et al* 1991, Enderle *et al* 1990b, c, a, Pilawa 1990). The result was that the terms of the two lowest multiplets $^5I_{8,7,6}$ and $^5F_{5,4,3,2}$ can be fitted very well by the one-electron crystal-field operator. At least five correlated crystal-field operators are additionally necessary in order to fit the crystal-field splittings of the terms $^3K_{8,7}$, $^5G_{6,5,4}$ and $^3H_{5,6}$ (Pilawa 1991a, b). In the present paper we report new measurements on the terms of $^5I_5$ and $^5I_4$ in the region 11 000 to 13 500 cm$^{-1}$. Our earlier studies of the term $^5I_5$ (Bischoff *et al* 1991, Enderle *et al* 1990b, c) led to relatively large discrepancies between the experimental and calculated energies of some of the crystal-field components. Thus we repeated the investigation and carried out polarized measurements of the Zeeman effect, which normally allow a definite determination of the crystal-field energies and crystal quantum numbers. Furthermore, we measured the crystal-field splittings of the term $^5I_4$, which have been unknown up to now. Hence, additional experimental data can be compared with crystal-field calculations.

## 2. Experimental details

The absorption spectra of $Ho^{3+}$ in $HoVO_4$, $HoAsO_4$, $HoPO_4$ and $(Ho_{0.1}, Y_{0.9})(OH)_3$ were measured in the near-infrared region (wavelengths 700–1100 nm) using a 3.4 m-Ebert grating spectrograph with automatic recording. Temperatures between 1.4 and 70 K and magnetic fields up to 4 T were available. In the range investigated the dispersion was 0.2 nm $mm^{-1}$. Taking 50 $\mu$m slits, the resolution was limited to about 0.5 $cm^{-1}$. The spectra were analysed using the selection rules valid for the point symmetries of the $Ho^{3+}$ sites in the various host lattices. The host lattices of $HoVO_4$, $HoAsO_4$ and $HoPO_4$ are tetragonal and the point symmetry of the $Ho^{3+}$ sites is $\bar{4}$2m. Therefore the crystal-field components of the $Ho^{3+}$ ions can be labelled by two crystal quantum numbers $\bar{\mu}$ and $\nu$, which describe the transformation properties acccording to $\bar{4}$ and 2, respectively (for details see Enderle *et al* (1990b)). The host latice of $(Ho_{0.1}, Y_{0.9})(OH)_3$ is hexagonal and the point symmetry of the $Ho^{3+}$ sites is approximately $\bar{6}$m2. Thus the crystal-field components can be labelled by the two crystal quantum numbers $\bar{\mu}$ and $S$, which are related to $\bar{6}$ and m, respectively (for details see Pilawa (1990)).

## 3. Experimental results

### 3.1. $Ho^{3+}$ in $HoVO_4$

*3.1.1.* $^5I_5$. The measurements on a diluted (Ho,Y)VO$_4$ crystal confirm our previous results in every detail (Enderle *et al* 1990b).

*3.1.2.* $^5I_4$. All crystal-field components could be assigned. The data are collected in table 1. From the lowest crystal-field component of the term $^5I_8$, transitions were found to the two doublets $\bar{\mu} = \pm1$ and to the singlet $\bar{\mu} = 2$, $\nu = 1$. Transitions from the first excited doublet at 20.7 $cm^{-1}$ were observed to all singlets $\bar{\mu} = 0$, the singlet $\bar{\mu} = 2$, $\nu = 1$ and the lowest doublet. The singlets $\bar{\mu} = 0$, $\nu = 0$ were ascertained by means of transitions from the accidentally coinciding excited doublet and singlet at 46.5 $cm^{-1}$. A transition from the doublet at 46.5 $cm^{-1}$ and a weak transition from the singlet $\bar{\mu} = 2$, $\nu = 0$ at 116.6 $cm^{-1}$ gave evidence for the singlet $\bar{\mu} = 0$, $\nu = 1$. Hence it is shown that the singlet $\bar{\mu} = 2$, $\nu = 1$ is nearly degenerate with the upper two singlets $\bar{\mu} = 0$. Additionally, an absorption line nearly 100 $cm^{-1}$ above the main group of absorption lines was interpreted as a transition from the second excited doublet of the ground term to the singlet $\mu = 2$, $\nu = 0$. In order to check the assignment of the crystal quantum numbers, measurements of the Zeeman effects at 1.4 K were carried out with the magnetic field applied either parallel to the twofold symmetry axis or perpendicular to the mirror plane of the host crystal. Thereby the crystal quantum numbers of the lowest singlet $\bar{\mu} = 0, \nu = 0$, the singlet $\bar{\mu} = 2$, $\nu = 0$ and the doublets could be verified. The range around the singlet $\bar{\mu} = 2$, $\nu = 1$ could not be unravelled. Therefore the spectrum of $Ho^{3+}$ in $(Ho_{0.01}, Dy_{0.99})VO_4$ was studied. Pure $DyVO_4$ shows a crystallographic distortion due to a cooperative Jahn–Teller effect below $T_D = 14.3$ K (Cooke *et al* 1970). By this the site symmetry of the rare-earth ions is reduced from $\bar{4}$2m to mm2. Thus below $T_D$ additional $Ho^{3+}$ transitions become observable (weakening of selection rules and mixing of the eigenfunctions, for further details see Enderle *et al* (1990b)). It turned out that the singlet $\bar{\mu} = 0$, $\nu = 0$ does indeed lie slightly above the singlet $\bar{\mu} = 2$, $\nu = 1$.

**Table 1.** Energies and crystal quantum numbers of the components of the term $^5I_4$ of Ho$^{3+}$. The term-dependent crystal-field parameters of table 2 were used to calculate the energies.

| Host crystal | Crystal quantum numbers | | Energy of component (cm$^{-1}$) | Calculated energy (cm$^{-1}$) |
|---|---|---|---|---|
| | $\bar{\mu}$ | $\nu$ | | |
| HoVO$_4$ | 0 | 0 | 13 197.5 | 13 197.2 |
| | ±1 | | 13 228.3 | 13 227.7 |
| | 0 | 1 | 13 315.3 | 13 317.2 |
| | 2 | 1 | 13 317.1 | 13 317.8 |
| | 0 | 0 | 13 319.5 | 13 317.4 |
| | ±1 | | 13 336.1 | 13 336.8 |
| | 2 | 0 | 13 472.8 | 13 472.1 |
| | | | | |
| HoAsO$_4$ | 0 | 0 | 13 192.1 | 13 192.3 |
| | ±1 | | 13 208.3 | 13 208.6 |
| | 0 | 1 | 13 289.6 | 13 289.3 |
| | 2 | 1 | 13 299.8 | 13 299.7 |
| | 0 | 0 | 13 308.3 | 13 310.3 |
| | ±1 | | 13 309.1 | 13 307.5 |
| | 2 | 0 | 13 395.4 | 13 395.9 |
| | | | | |
| HoPO$_4$ | 0 | 0 | 13 232.9 | 13 231.9 |
| | ±1 | | 13 241.8 | 13 240.8 |
| | 0 | 1 | 13 286.8 | 13 286.9 |
| | 0 | 0 | 13 331.4 | 13 330.3 |
| | 2 | 1 | 13 357.2 | 13 356.8 |
| | ±1 | | — | 13 361.3 |
| | 2 | 0 | 13 449.6 | 13 448.6 |
| | | | | |
| | $\bar{\mu}$ | $S$ | | |
| (Ho,Y)(OH)$_3$ | 3 | 1 | 13 169.2 | 13 170.3 |
| | ±2 | | 13 293.8 | 13 291.8 |
| | 0 | 0 | — | 13 344.0 |
| | 3 | 0 | 13 356.7 | 13 355.8 |
| | ±1 | | — | 13 367.7 |
| | ±2 | | 13 428.2 | 13 429.5 |

## 3.2. Ho$^{3+}$ in HoAsO$_4$

### 3.2.1. $^5I_5$.
Here again the results of our former investigation (Enderle *et al* 1990c) are fully confirmed.

### 3.2.2. $^5I_4$.
All components were assigned from measurements at different temperatures. The data are listed in table 1. One $\pi$-polarized and three $\sigma^+$-polarized transitions were observed at 1.4 K. These transitions give the energies of the lowest doublet and of the singlets $\bar{\mu} = 0$. Transitions from the first excited singlet $\bar{\mu} = 0$, $\nu = 0$ at 7.7 cm$^{-1}$ were observed to both doublets and to the singlet $\bar{\mu} = 2$, $\nu = 1$. The singlet $\bar{\mu} = 2$, $\nu = 0$ could only be assigned by one transition from the first excited doublet at 27.8 cm$^{-1}$. The succession of the different singlets and doublets is the same as that found for Ho$^{3+}$ in HoVO$_4$. The splitting factor of the lowest doublet is $1.25 \pm 0.25$.

## 3.3. Ho$^{3+}$ in HoPO$_4$

### 3.3.1. $^5I_5$.
This term was analysed for the first time by Bischoff *et al* (1991). The

comparatively large differences between the experimental and the calculated crystal-field energies caused us to repeat the investigation and to record the spectra with linear and circular polarization at 1.4 K. These spectra are reproduced in figure 1. Its analysis confirms our previous results and the published data. Additionally we measured the splitting factors and obtained the values $-5.4 \pm 0.6$, $+2.3 \pm 0.2$ and $-0.4 \pm 0.1$ for the doublets at 11 215.9, 11 234.5 and 11 290.7 cm$^{-1}$, respectively.
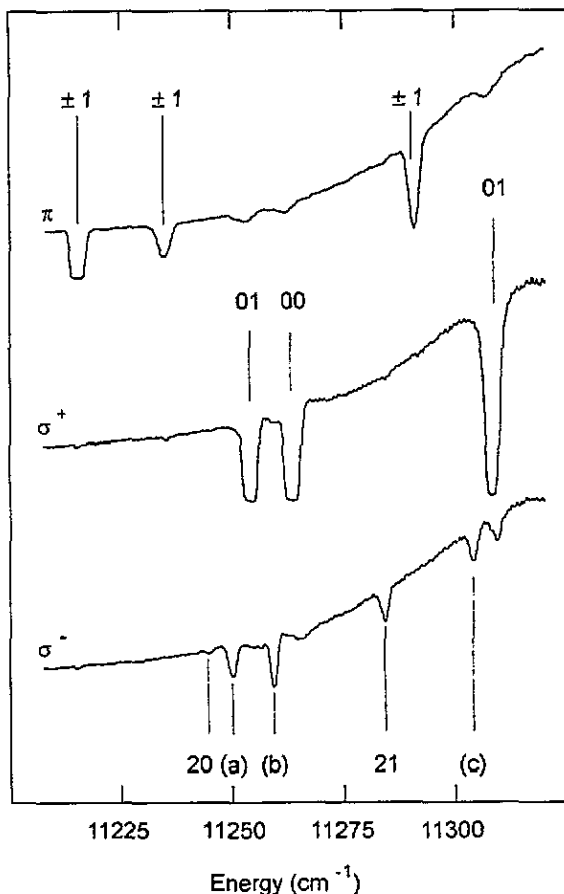


**Figure 1.** Transitions to the term $^5I_5$ of Ho$^{3+}$ in HoPO$_4$ at 1.4 K. $\sigma^+$- and $\sigma^-$-polarization, $B = 1$ T along the crystal $c$ axis; $\pi$-polarization, $B = 0$. The labels are the crystal quantum numbers $\bar{\mu}$ and $\nu$ of the components of $^5I_5$. Lines (a), (b) and (c) correspond to transitions from the upper Zeeman components of the ground-state doublet to the singlets $\bar{\mu} = 0$.

### 3.3.2. $^5I_4$.

The spectrum at 1.4 K showed only three $\sigma^+$-polarized absorptions which correspond to transitions from the ground doublet to the singlets $\bar{\mu} = 0$. At temperatures around 70 K further absorptions could be observed. Transitions from the first excited singlet $\bar{\mu} = 0$, $\nu = 0$ at 71.7 cm$^{-1}$ and from the first excited doublet at 89.2 cm$^{-1}$ were found to the lowest doublet and to the singlet $\bar{\mu} = 2$, $\nu = 1$. Only one transition was noticed that might establish the position of the singlet $\bar{\mu} = 2$, $\nu = 0$. We assume that this is a transition
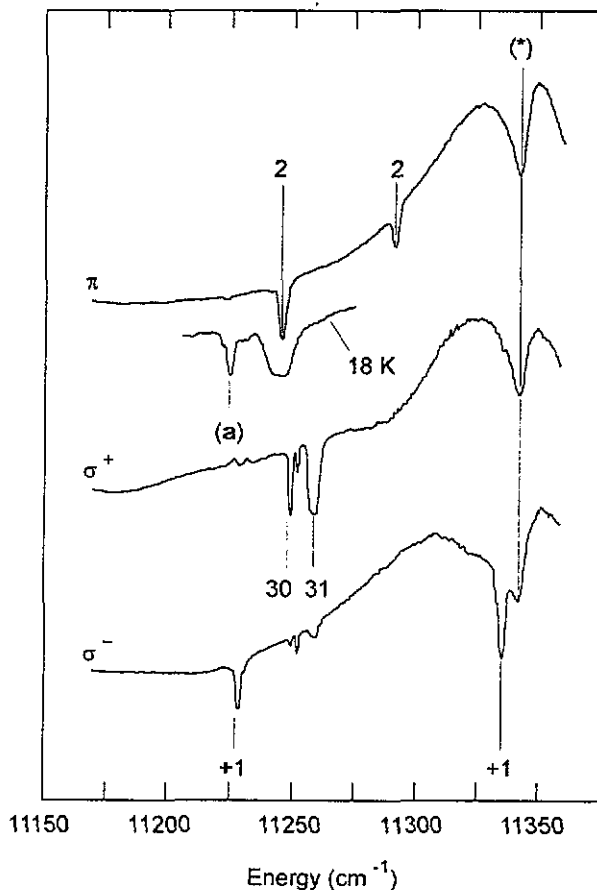
**Figure 2.** Transitions to the term $^5I_5$ of $Ho^{3+}$ in $(Ho_{0.1},Y_{0.9})(OH)_3$ at 1.4 K. $\sigma^+$- and $\sigma^-$-polarization, $B = 2$ T along the crystal $c$ axis; $\pi$-polarization, $B = 0$. The labels are the crystal quantum numbers $\bar{\mu}$ and $S$ of the components of $^5I_5$. A part of the spectrum at 18 K in $\pi$-polarization is included. Line (a) is caused by the transition from the first excited singlet $\bar{\mu} = 0$, $S = 0$ at 71.7 cm$^{-1}$ to the singlet $\bar{\mu} = 3$, $S = 0$. The line marked (*) belongs to the spectrum of the Xe lamp used.

from the first excited doublet of the ground term. This assignment was made in analogy to that used for $Ho^{3+}$ in $HoVO_4$ and $HoAsO_4$. No absorption line could unequivocally be assigned to a transition to the upper doublet. The data are collected in table 1.

## 3.4. Ho³⁺ in (Ho₀.₁,Y₀.₉)(OH)₃

3.4.1. $^5I_5$. Since the experimental results found by Bischoff *et al* (1991) seriously disagree with crystal-field calculations we supplemented this work by measuring the Zeeman effect. Figure 2 shows the polarized spectra at low temperatures. The second crystal quantum number of the singlets $\bar{\mu} = 3$ was verified by measurements at 18 K, where we found the transition from the first excited singlet $\bar{\mu} = 0$, $S = 0$ at 11.3 cm$^{-1}$ to the singlet $\bar{\mu} = 3$, $S = 0$. The splitting factors were determined to be $-4.5 \pm 0.1$ and $+1.3 \pm 0.4$ for the doublets $\bar{\mu} = \pm 1$ at 11 239.1 and 11 319.5 cm$^{-1}$, respectively, and to be $-2.8 \pm 0.1$ and $+1.0 \pm 0.3$ for the doublets $\bar{\mu} = \pm 2$ at 11 256.9 and 11 292.9 cm$^{-1}$, respectively.

*3.4.2.* $^5I_4$. The energies of the doublets $\bar{\mu} = \pm 2$ and the singlets $\bar{\mu} = 3$ could be determined directly from the spectra taken at 1.4 K. Measurements at 20 K allowed us to fix the crystal quantum number $S$ of the singlets $\bar{\mu} = 3$. But no hint of the doublet $\bar{\mu} = \pm 1$ and the singlet $\bar{\mu} = 0$, $S = 0$ could be found. The data are presented in table 1.

## 4. Crystal-field calculation

In a previous investigation of the multiplet $^5I$ we carried out a fit of the crystal-field parameters (Bischoff *et al* 1991) and we found that the experimental results generally could be well reproduced. Indeed, crystal-field calculations were used to analyse the complicated spectra taken at high temperatures. Nevertheless we noticed that rather big differences occur, especially for the crystal-field components of the term $^5I_5$. We have now determined the term-dependent parameters $a_q^{(k)}(\gamma J)$ (Pilawa 1991a, b) of the terms $^5I_{7,6,5,4}$. A crystal-field matrix was diagonalized which included all terms of the multiplets $^5F$ and $^5I$, in order to account for $J$-mixing effects (for more details see Bischoff *et al* (1991)). In agreement with our previous publications, we used the following parameter values to calculate the wavefunction of the free $Ho^{3+}$ ion: $E^1 = 6698.4$ cm$^{-1}$, $E^2 = 28.8$ cm$^{-1}$, $E^3 = 630.2$ cm$^{-1}$, $\zeta = -2086.7$ cm$^{-1}$, $\alpha = 31.2$ cm$^{-1}$, $\beta = -992.6$ cm$^{-1}$ and $\gamma = 0$. The results of the fits are collected in table 2 for $Ho^{3+}$ in $HoVO_4$, $HoAsO_4$, $HoPO_4$ and $(Ho_{0.1},Y_{0.9})(OH)_3$. The mean values for the crystal-field parameters agree within the rms deviation with the parameter values obtained by Bischoff *et al* (1991). It was not possible to achieve a satisfactory fit for the term $^5I_5$. This is especially true for $Ho^{3+}$ in $HoPO_4$ and in $(Ho_{0.1},Y_{0.9})(OH)_3$. The rms deviation between the measured and calculated crystal-field energies is nearly as big as for the term $^5G_6$ (Pilawa 1991a), although the overall splitting of the $^5I_5$ is smaller by a factor of one-third.

The variation of the crystal-field parameters for $Ho^{3+}$ in $HoVO_4$, $HoAsO_4$ and $HoPO_4$ is comparable to that found for the terms of the multiplet $^5F$ (Pilawa 1991a). However, for $Ho^{3+}$ in $(Ho_{0.1},Y_{0.9})(OH)_3$ the variations are extremely large and do not match with the fact that the $^5I$ multiplet is an almost pure Russell–Saunders multiplet.

## 5. Conclusion

The absorption spectra of $Ho^{3+}$ in $HoVO_4$, $HoAsO_4$, $HoPO_4$ and $(Ho_{0.1},Y_{0.9})(OH)_3$ in the near-infrared region and their Zeeman effect have been studied. Nearly all crystal-field components of the term $^5I_4$ could be determined. Only one doublet is missing in $HoPO_4$ and two components (a doublet and a singlet) in $(Ho_{0.1},Y_{0.9})(OH)_3$. The crystal-field components of the term $^5I_5$ could be further confirmed by recording linearly and circularly polarized spectra at temperatures between 1.4 and 70 K. Now most of the crystal-field components of the multiplet $^5I$ are known for $Ho^{3+}$ in these host lattices.

Since the free-ion wavefunctions of the $^5I$ multiplet are nearly pure states with $L = 6$ and $S = 2$, one expects that the crystal-field splittings of all terms of this multiplet can be calculated by using just one set of crystal-field parameters. Our analysis reveals that this is true only approximately. The crystal-field parameters vary from term to term. Although the variation is small compared with those found for the multiplets $^5G$ and $^3K$, it nevertheless shows the influence of the electron correlation on the crystal-field interaction.

An unusual situation is found in the case of the term $^5I_5$. Normally the crystal-field splittings can be fitted quite well by means of term-dependent parameters. However, for

**Table 2.** Term-dependent crystal-field parameters $a_q^{(k)}(\gamma J)$ of Ho$^{3+}$ for the terms of the multiplet $^5$I. $\sigma$ denotes the rms deviation that can be achieved by a fit of the calculated crystal-field energies to the measured ones. All figures have the units cm$^{-1}$.

| | | $^5$I$_7$ | $^5$I$_6$ | $^5$I$_5$ | $^5$I$_4$ | Average values for $a_q^{(k)}$ |
|---|---|---|---|---|---|---|
| HoVO$_4$ | $\sigma$ | 1.3 | 2.0 | 1.8 | 1.2 | |
| | $a_0^{(2)}$ | −185 | −136 | −103 | −132 | −138 ± 35 |
| | $a_0^{(4)}$ | 337 | 220 | 384 | 435 | 343 ± 90 |
| | $a_4^{(4)}$ | −785 | −793 | −605 | −762 | −733 ± 88 |
| | $a_0^{(6)}$ | −728 | −625 | −729 | −741 | −711 ± 60 |
| | $a_4^{(6)}$ | 58 | 213 | 295 | 194 | 188 ± 64 |
| HoAsO$_4$ | $\sigma$ | 0.6 | 1.8 | 2.1 | 0.5 | |
| | $a_0^{(2)}$ | −37 | −28 | −30 | −12 | −26 ± 12 |
| | $a_0^{(4)}$ | 67 | −17 | 48 | 103 | 50 ± 50 |
| | $a_4^{(4)}$ | −717 | −671 | −579 | −672 | −660 ± 58 |
| | $a_0^{(6)}$ | −679 | −680 | −625 | −628 | −653 ± 31 |
| | $a_4^{(6)}$ | −51 | 31 | 61 | −32 | 2 ± 53 |
| HoPO$_4$ | $\sigma$ | 0.9 | 1.4 | 3.5 | 0.9 | |
| | $a_0^{(2)}$ | 364 | 352 | 362 | 348 | 350 ± 21 |
| | $a_0^{(4)}$ | 41 | −8 | 6 | 104 | 39 ± 56 |
| | $a_4^{(4)}$ | −707 | −685 | −561 | −672 | −652 ± 64 |
| | $a_0^{(6)}$ | −660 | −758 | −740 | −682 | −712 ± 45 |
| | $a_4^{(6)}$ | −97 | 67 | 2 | −52 | −20 ± 84 |
| (Ho,Y)(OH)$_3$ | $\sigma$ | 1.2 | 0.9 | 3.6 | 1.1 | |
| | $a_0^{(2)}$ | 452 | 495 | 517 | 142 | 414 ± 150 |
| | $a_0^{(4)}$ | −523 | −608 | −616 | −597 | −590 ± 45 |
| | $a_0^{(6)}$ | −638 | −656 | −555 | −421 | −566 ± 109 |
| | $a_6^{(6)}$ | 623 | 368 | −75 | 646 | 390 ± 335 |

the term $^5$I$_5$ of Ho$^{3+}$ in HoPO$_4$ and (Ho$_{0.1}$,Y$_{0.9}$)(OH)$_3$ the rms deviations between the measured and calculated crystal-field components remain extremely large, even if a fit of term-dependent crystal-field parameters is carried out. This result can indicate that tensor operators of rank $k = 8$ or even higher should be included in the crystal-field description. Such an extension is certainly possible in the scope of the theory of the correlated crystal field (Bishton and Newman 1970).

## Acknowledgment

## References

Bischoff H, Pilawa B, Kasten A and Kahle H G 1991 *J. Phys.: Condens. Matter* **3** 10057–64

Bishton S S and Newman D J 1970 *J. Phys. C: Solid State Phys.* **3** 1753–61

Cooke A H, Ellis C J, Gehring K A, Leask M J M, Martin D M, Wanklyn B M, Wells M R and White R L 1970
    *Solid State Commun.* **8** 689–92

Enderle M, Pilawa B and Kahle H G 1990a *J. Phys.: Condens. Matter* **2** 4711–15

Enderle M, Pilawa B, Schlaphof W and Kahle H G 1990b *J. Phys.: Condens. Matter* **2** 4685–700

Enderle M, Pilawa B, Schwab M and Kahle H G 1990c *J. Phys.: Condens. Matter* **2** 4701–10

Pilawa B 1990 *J. Phys.: Condens. Matter* **2** 5555–62

—— 1991a *J. Phys.: Condens. Matter* **3** 655–66

—— 1991b *J. Phys.: Condens. Matter* **3** 667–73

Rajnak K and Krupke W F 1967 *J. Chem. Phys.* **46** 3532–41

Rajnak K and Wybourne B G 1964 *J. Chem. Phys.* **41** 565–9