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# Orthorhombic standardization of spin-Hamiltonian parameters for transition-metal centres in various crystals

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**Abstract.** Several sets of non-standard zero-field splitting (ZFS) parameters in the spin Hamiltonian (SH) for transition-metal ions at orthorhombic or lower symmetry sites in various crystals have been revealed by a recent literature survey. The standardization limits the ratio of the orthorhombic ZFS parameters:  $0 \leq E/D \leq 1/3$  (conventional) and  $0 \leq B_2^2/B_2^0 = b_2^2/b_2^0 \leq 1$  (the extended Stevens (ES) notation). Based on the superposition model it is shown that the 'maximum rhombicity' limit is valid not only in the *effective* SH sense but also in the crystallographic sense. Using the computer package CST the non-standard orthorhombic ZFS parameter sets given originally in various parameter and operator notations, units and conventions for the axis systems are standardized and presented in a unified way in the ES notation  $b_k^q$  and units of  $10^{-4} \text{ cm}^{-1}$ . This enables a direct comparison with the available data for similar ion/host systems. The standardization reveals several inconsistencies in interpretation of earlier EPR results.

## 1. Introduction

A recent literature survey indicates a number of non-standard SH parameter sets expressed in different notations and formats. This hinders direct comparison of data and may lead to misinterpretation of results. The recently developed [1] computer package CST, for *conversions, standardization and transformations* of the spin Hamiltonian (SH) and crystal field (CF) Hamiltonian as well as for transformations of the electronic Zeeman terms [2], is employed to standardize and present in a unified way the *non-standard* zero-field splitting (ZFS) parameters from different sources. The standardization of an orthorhombic SH [3, 4] consists in confining, by a proper choice of the axis system, the ratio of the orthorhombic ZFS parameters in the *conventional* notation [2],  $E/D \equiv \lambda$ , to the range  $(0, \pm 1/3)$  [5–7], or equivalently in the extended Stevens (ES) notation [2, 8],  $B_2^2/B_2^0 = b_2^2/b_2^0 = \lambda'$ , to the range  $0 \leq \lambda' \leq 1$  [5, 9–11].

In this paper the standardization and notations used are outlined in section 2. Structural implications of standardization are discussed using superposition model in section 3. In section 4 applications of standardization to various transition-metal centres described by the orthorhombic SH are considered. Applications to transition-metal as well as rare-earth ion centres exhibiting monoclinic or triclinic symmetry will be dealt with in forthcoming papers.

## 2. Standardization of orthorhombic ZFS Hamiltonian

In the extended Stevens (ES) operators [8] the *effective* ZFS Hamiltonian for orthorhombic symmetry is given as (for references, see, e.g. [2]):

$$\begin{aligned}\mathcal{H}_{ZFS} &= B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6 \\ &= \sum_{kq} B_k^q O_k^q(S_x, S_y, S_z) = \sum_{kq} f_k b_k^q O_k^q(S_x, S_y, S_z)\end{aligned}\quad (1)$$

where  $f_k = 1/3, 1/60$  and  $1/1260$  for  $k = 2, 4$  and  $6$  respectively. The *conventional*  $D$  and  $E$  parameters [3, 4, 7, 8] are related to those in the ES notation [8] as [2, 5]:

$$D = 3B_2^0 = b_2^0 \quad E = B_2^2 = 1/3b_2^2. \quad (2)$$

Similarly the fourth-order conventional orthorhombic ZFS parameters  $a, F$  and  $K$  are related to those in the ES notation as:  $B_4^0 = a/120 + F/180$ ,  $B_4^4 = a/24$  and  $B_4^2 = K$  [2]. Conversions between various other notations are dealt with in [1, 2].

$\mathcal{H}_{ZFS}$  in equation (1) has an intrinsic property [5], namely, that by a proper choice of the axis system  $(x, y, z)$  the ratio  $E/D \equiv \lambda$  and  $B_2^2/B_2^0 = b_2^2/b_2^0 = \lambda'$  can be confined to the range  $(0, \pm 1/3)$  and  $0 \leq \lambda' \leq \pm 1$ , respectively. Two conventions on the choice of the  $\mathbf{D}$  tensor components exist in the literature: (i)  $|D_{xx}| \leq |D_{yy}| \leq |D_{zz}|$ , i.e.  $0 \leq \lambda \leq 1/3$  [3, 6, 7] and (ii)  $|D_{yy}| \leq |D_{xx}| \leq |D_{zz}|$  [4], i.e.  $-1/3 \leq \lambda \leq 0$ . The convention (i) is most used in EPR studies of transition-metal ions. The works on the transformation properties of the ES operators [8] have enabled standardization of the fourth- and sixth-order ZFS (and CF) terms [5] as well as of the monoclinic CF [9] and ZFS Hamiltonian [10].

Authors unaware of the standardization properties of the SH, when extracting the ZFS parameter values from experimental EPR data, use an unrestricted approach resulting in values of  $\lambda$  ( $\lambda'$ ) outside the standard range. A recent literature survey indicates a number of non-standard SH parameter sets expressed in various formats. This hinders direct comparison of data and may lead to misinterpretation of results. Hence, a computer package CST [1] has been developed to enable efficient standardization of the ZFS parameters expressed in any notation as well as of the electronic Zeeman terms for orthorhombic and monoclinic symmetry. The standardization formulas [5] for the ZFS (or CF) parameters  $B_k^q$  (ES) or  $b_k^q$  (ES), in equation (1), were derived for the transformations from the original axis system  $S_1(x y z)$  to  $S_i$ ,  $i = 2$  to  $6$ , defined as follows:  $S_2[x z - y]$ ,  $S_3[y x - z]$ ,  $S_4[z x y]$ ,  $S_5[y z x]$  and  $S_6[z y - x]$ . For other notations reviewed in [2] appropriate conversion options are built into the CST package [1], whereas conversions to the *reference* ES notation [8] are carried out automatically. The *orthorhombic* type standardization includes three sub-options: (i) automatic standardization if the ratio  $\lambda'$  ( $\lambda$  or equivalent) is outside the range  $(0, 1)$ , (ii) application of a specified standardization transformation  $S_i$  ( $i = 2$  to  $6$ ) [5] and (iii) calculation of the standardization errors [11].

For the electronic Zeeman term in the SH [1, 2, 5, 8] the standardization transformations  $S_i$ ,  $i = 2-6$ , result only in re-labelling of the  $g_{ij}$  components ( $i, j = x, y, z$ ). The explicit results for the transformed  $[g_{ij}]$  are given in [1, 8]. One must be careful not to confuse the original  $\{g_{ij}\}$  and the transformed  $[g_{ij}]$  components. For example, the standardization transformation  $S_4$  yields:  $[g_x] = \{g_y\}$ ,  $[g_y] = \{g_z\}$ ,  $[g_z] = \{g_x\}$ . The same result can be obtained using the GTRANS module [1] with the values of the angles  $(\phi_1, \theta_1)$  and  $(\phi_2, \theta_2)$  corresponding to the transformation  $S_4$  [8].

### 3. Structural implications of orthorhombic standardization

The major physical implication of standardization concerns the structural aspects. The ratio  $E/D \equiv \lambda$  defines the 'rhombicity' parameter, which measures the deviation from axial symmetry, and its value may be restricted to the range  $0 \leq \lambda \leq 1/3$  [3-7]. A number of authors noted that  $\lambda = 0$  represents axial symmetry, whereas the maximum possible rhombicity is characterized by  $\lambda = 1/3$ . However, since we deal with the *effective* Hamiltonian  $\mathcal{H}_{ZFS}$

[2], equation (1), it may appear that the ZFS parameter ratio describes the ‘rhombicity’ in the *effective* and not crystallographic sense. Below we use the superposition model [12], which provides direct relationships between the ZFS parameters and the structural ones, to show that the ‘maximum rhombicity’ limit:  $E/D = 1/3$  or  $B_2^2/B_2^0 = b_2^2/b_2^0 = 1$ , is valid not only in the *effective* SH sense but also in the crystallographic sense.

For illustration we consider a  $3d^4$  or  $3d^6$  ion at an octahedral site having the first kind of rhombic symmetry [12] with the three mutually perpendicular axes  $x$ ,  $y$  and  $z$  directed towards the ligands. With the ligands located in pairs along the axes  $+x$ ,  $+y$  and  $+z$  at a distance from the central ion denoted  $R_2$ ,  $R_3$  and  $R_1$ , respectively, we obtain the superposition model formulas as follows [12]:

$$B_2^0 = \pm \bar{A}_2 \frac{2}{21} \left[ \left( \frac{R_0}{R_2} \right)^{t_2} + \left( \frac{R_0}{R_3} \right)^{t_2} - 2 \left( \frac{R_0}{R_1} \right)^{t_2} \right] \quad (3a)$$

$$B_2^2 = \pm \bar{A}_2 \frac{2}{7} \left[ \left( \frac{R_0}{R_3} \right)^{t_2} - \left( \frac{R_0}{R_2} \right)^{t_2} \right]. \quad (3b)$$

The positive sign in equations (3) applies to  $3d^6$  ions, whereas the negative sign to  $3d^4$  ions [12]. The intrinsic parameters  $\bar{A}_2$  and the power law exponent  $t_2$  depend on the properties of the central ion and ligands. Note that the case  $R_1 = R_2 = R_3$  corresponds to cubic symmetry and then  $B_2^0 = B_2^2 = 0$ , whereas the case  $R_1 \neq R_2 = R_3$  corresponds to tetragonal symmetry and then  $B_2^2 = 0$ . For orthorhombic symmetry two cases are crucial: (i)  $B_2^0 \equiv B_2^2$ , i.e.  $\lambda' \equiv 1$ , and (ii)  $3B_2^0 \equiv B_2^2$ , i.e.  $\lambda' \equiv 3$ . Using the relations for the transformations  $S_2$  and  $S_5$  [5], which yield  $\lambda'$  in the standard range for the case (i) and (ii), respectively, one obtains the formulas for the transformed parameters  $[B_2^0]$  and  $[B_2^2]$  which are identical with those in equations (3) after replacement of  $(R_1, R_2, R_3)$  by  $(R_3, R_2, R_1)$  and  $(R_3, R_1, R_2)$ , respectively. Thus based on the structural data and the superposition model [12] one can limit the values of  $B_2^0$  and  $B_2^2$  to the standard range by an appropriate re-labelling of the ligand–central-ion distances and, correspondingly, of the axes. This conclusion is also true for any ion and kind of rhombic symmetry within the framework of the superposition model. Hence the ‘maximum rhombicity’ limit is valid not only in the *effective* SH sense but also in the crystallographic sense.

#### 4. Results and discussion

The non-standard SH parameter sets identified in our recent literature survey are standardized using the CST package [1]. In tables 1 to 6 for each ZFS parameter set we list: the original notation and units (denoted OU), the standardized parameters  $b_k^q$ (ES) [2, 8] in units of  $10^{-4} \text{ cm}^{-1}$  (with errors [11], if available), the ratio  $\lambda'$  ( $\lambda$ ) and the required standardization transformation  $S_i$  (denoted TR). Wherever available, the definition of the original axis system and conventions used are given in the text.

##### 4.1. Tutton salts

Table 1 contains ZFS parameters for  $\text{Mn}^{2+}$  in Tutton salts:  $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (ZASH),  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (FASH),  $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (MASH) [13],  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (NiASH) and  $\text{Cd}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (CdASH) [14], having monoclinic structure and triclinic  $C_i$  site symmetry of  $\text{M}^{2+}$  [15]. An orthorhombic SH has been used in least-squares fitting [13–15]. The orthorhombic axes ( $x$   $y$   $z$ ) have been defined with respect to the maximum spread of the extrema in EPR spectra at room temperatures (RT) with the convention  $|D_z| > |D_x| > |D_y|$  [13, 14]. The determination of the ‘magnetic’ axes from EPR

spectra [13–15] is doubtful for monoclinic or triclinic sites as discussed in [10] due to the non-coincidence of extrema [16]. Moreover, since at low temperatures the overall line separation changes [13, 14], using the RT axis system [13, 14] results in non-standard  $b_k^q$  at low  $T$ . The variation of the ‘magnetic’ axes and SH parameters with  $T$  may indicate the occurrence of a structural phase transition. The discrepancies between data [13–15, 17] may originate from the orthorhombic approximation or different axis systems and conventions used. Had a monoclinic SH and crystallographic axis system been used in fitting, a meaningful inter-comparison of data [13–15, 17] (see also more recent data on  $\text{Mn}^{2+}$  in Tutton salts [18, 19]) would be possible. Instead, implications of standardization are considered.

Table 1 reveals that  $b_2^0$  changes sign from negative [13, 14] to positive after standardization. For  $\text{Mn}^{2+}$  in ZASH, FASH and MASH as the temperature decreases  $|b_2^2|$  increases and becomes slightly greater than  $|b_2^0|$  at low  $T$  [13], which yields  $|\lambda' = b_2^2/b_2^0| \approx 1$ . For  $\text{Mn}^{2+}$  in NiASH and CdASH at low  $T$  [14]  $\lambda' \propto (-3, -1)$  and requires the transformation  $S_4$ , except for  $\text{Mn}^{2+}:\text{NiASH}$  at 5 K, where  $\lambda' \propto (-\infty, -3)$  and requires  $S_6$ . Importantly, for  $\text{Mn}^{2+}:\text{NiASH}$  at 5 K and 85 K the error is larger than the standardized parameter  $b_4^0$  and the standardized  $\lambda'$  (85 K) is 10 times larger than  $\lambda'$  (5 K).

The dependence of the signs and magnitudes of SH parameters on the choice of the axis system and one transformation ( $S_5$  in our notation [5]) has been considered in [15]. A related aspect is the selection of the initial values of the dominant SH parameters used in fitting procedures [15]. Using  $b_k^q$  obtained from high  $T$  data for  $\text{Mn}^{2+}$  in Tutton salts [13, 14] as the initial  $b_k^q$  for low  $T$  fitting yields fitted  $b_k^q$  overall close to those at high  $T$  but with  $|b_2^2| \geq |b_2^0|$ . Had another initial  $b_k^q$  set been used for fitting, a  $b_k^q$  set close to the standardized one in table 1 would be obtained. For illustration, for  $\text{Mn}^{2+}$  in ZASH [13] we select a non-standard  $b_k^q$  set at 85 K and a standard one at 295 K and list in table 2 all *equivalent* data sets transformed using each  $S_i$ . Table 2 shows how the signs of ZFS parameters change with the axis system and hence puts in a different perspective the controversy [13–15, 17–19] on the absolute sign of  $b_2^0$ .

Each transformed data set in table 2 lies in a different region of the parameter space, yet all these sets are *equally valid*. Using each of the parameter sets lying in a different region of the parameter space as an initial set for fitting would yield several independently fitted, *yet mutually correlated*, data sets. Transformations to the same (e.g., standard) range should yield very close parameter values for all *correlated* sets, provided that each fitted set corresponds to an equivalent global minimum in the parameter space. Thus having two or more independently fitted sets may improve the reliability of the final ZFS parameters and help to discriminate between local and global minima in the parameter space used for fitting. These features have been utilized in the *multiple correlated fitting technique* proposed in [9, 10].

## 4.2. $\text{AB}_2$ compounds

4.2.1.  $\text{Mn}^{2+}$  in  $\text{MgF}_2$ . Although no explicit form of orthorhombic SH was given in [20] the parameters were denoted  $b_2^0 = D$  and  $b_2^2 = 3E$  as in the usual convention [2]. Three non-standard ( $D$ ,  $E$ ) sets were given [20]: (I) recalculated from the experimental standard values [21], (II) calculated using the superposition model and (III) calculated using the spin-orbit mechanism. The fourth-order ZFS parameters have not been considered in [20], unlike in [21] where  $b_4^q$  are listed. The standardized  $b_2^0$  and  $b_2^2$  are given in table 3. The set (I) after standardization corresponds to that for  $\text{Mn}^{2+}:\text{MgF}_2$  at 290 K [21] apart from the sign of  $b_2^2$ . The non-standard  $D$  and  $E$  [20] are due to the choice of the co-ordinate system B, whereas the standard set is given in the system A (defined in figure 1 of [20]). The positive sign of  $b_2^2$  after the transformation  $S_5$  is due to the choice of the convention of positive  $\lambda$  [5].

**Table 1.** The original and standardized ZFS parameters  $b_k^0$  in the ES notation, including the errors, for  $\text{Mn}^{2+}$  in Tutton salts. The abbreviated host names are explained in the text.

Ion: host	Set	OU	Original parameters										Standardized parameters ( $10^{-4} \text{ cm}^{-1}$ )										Ref.
			$b_2^0$	$b_2$	$b_4^0$	$b_4$	$b_4^0/b_2^0$	$b_4$	$b_2^0/b_4^0$	TR	$b_2^0$	$b_2$	$b_4^0$	$b_4$	$b_4^0/b_2^0$	$b_4$	$b_2^0/b_4^0$						
$\text{Mn}^{2+}$ :ZASH	4.2 K	GHz	-0.738 $\pm 0.001$	0.833 $\pm 0.002$	0.004 $\pm 0.001$	-0.042 $\pm 0.008$	0.028 $\pm 0.010$	-1.13	$S_4$	262.0 $\pm 0.4$	230.3 $\pm 0.6$	3.4 $\pm 0.6$	5.7 $\pm 2.3$	-5.3 $\pm 2.8$	0.88	[13]							
	85 K		-0.726 $\pm 0.001$	0.863 $\pm 0.002$	0.005 $\pm 0.001$	0.040 $\pm 0.011$	0.102 $\pm 0.011$	-1.19	$S_4$	265.0 $\pm 0.4$	219.3 $\pm 0.6$	3.2 $\pm 0.7$	-19.5 $\pm 2.7$	23.2 $\pm 3.6$	0.83								
$\text{Mn}^{2+}$ :FASH	4.5 K	GHz	-0.727 $\pm 0.001$	0.824 $\pm 0.002$	0.009 $\pm 0.001$	-0.051 $\pm 0.009$	0.161 $\pm 0.009$	-1.13	$S_4$	258.7 $\pm 0.4$	226.3 $\pm 0.6$	9.9 $\pm 0.6$	-10.8 $\pm 2.3$	5.0 $\pm 3.0$	0.87	[13]							
	60 K		-0.719 $\pm 0.002$	0.865 $\pm 0.004$	0.002 $\pm 0.001$	0.019 $\pm 0.010$	0.062 $\pm 0.017$	-1.2	$S_4$	264.2 $\pm 0.8$	215.5 $\pm 1.2$	3.6 $\pm 0.8$	-5.5 $\pm 3.4$	4.2 $\pm 3.3$	0.82								
$\text{Mn}^{2+}$ :MASH	4.5 K	GHz	-0.731 $\pm 0.001$	0.803 $\pm 0.001$	0.004 $\pm 0.001$	-0.007 $\pm 0.016$	0.090 $\pm 0.015$	-1.1	$S_4$	255.8 $\pm 0.4$	231.8 $\pm 0.6$	4.5 $\pm 0.9$	-10.5 $\pm 3.7$	7.6 $\pm 4.9$	0.91	[13]							
	29 K		-0.723 $\pm 0.001$	0.811 $\pm 0.002$	0.002 $\pm 0.001$	-0.007 $\pm 0.012$	0.001 $\pm 0.013$	-1.12	$S_4$	255.8 $\pm 0.4$	226.5 $\pm 0.6$	3.4 $\pm 0.7$	14.7 $\pm 3.1$	-19.6 $\pm 3.8$	0.88								
$\text{Mn}^{2+}$ :NiASH	5 K	GHz	-0.377 $\pm 0.023$	1.242 $\pm 0.022$	-0.300 $\pm 0.029$	-1.036 $\pm 0.118$	-0.051 $\pm 0.031$	-3.29	$S_6$	270 $\pm 5.3$	18.5 $\pm 12.1$	3.5 $\pm 6.3$	68.9 $\pm 31.6$	-742.3 $\pm 54.6$	0.7	[14]							
	85 K		-0.633 $\pm 0.051$	0.855 $\pm 0.049$	-0.112 $\pm 0.058$	-0.849 $\pm 0.278$	-0.405 $\pm 0.101$	-1.35	$S_4$	248.2 $\pm 11.8$	174.1 $\pm 26.8$	4.50 $\pm 14.3$	115.7 $\pm 69.1$	-428.1 $\pm 117.3$	0.07								
$\text{Mn}^{2+}$ :CdASH	5 K	GHz	-0.715 $\pm 0.001$	0.863 $\pm 0.002$	0.002 $\pm 0.001$	0.010 $\pm 0.013$	0.035 $\pm 0.013$	-1.21	$S_4$	263.2 $\pm 0.4$	213.8 $\pm 0.6$	1.3 $\pm 0.8$	-5.8 $\pm 3.2$	7.3 $\pm 4.1$	0.81	[14]							
	85 K		-0.697 $\pm 0.001$	0.875 $\pm 0.002$	0.002 $\pm 0.001$	0.009 $\pm 0.009$	0.073 $\pm 0.011$	-1.26	$S_4$	262.2 $\pm 0.4$	202.8 $\pm 0.6$	2.9 $\pm 0.6$	-12.0 $\pm 2.5$	8.6 $\pm 3.0$	0.77								

**Table 2.** Values of the ZFS parameters  $b_k^q$  in the ES notation for the  $\text{Mn}^{2+}$  ZASH under different  $S_i$  transformations in  $[10^{-4} \text{ cm}^{-1}]$ .  $S_1$  denotes the original values [13] converted from GHz to  $10^{-4} \text{ cm}^{-1}$ .

$S_i$	Nonstandard at 75 K						Standard at 295 K					
	$b_2^0$	$b_2^2$	$b_4^0$	$b_4^2$	$b_4^4$	$b_2^2/b_2^0$	$b_2^0$	$b_2^2$	$b_4^0$	$b_4^2$	$b_4^4$	$b_2^2/b_2^0$
$S_1$	-242.2	287.9	1.7	13.3	34.0	-1.2	-236.8	197.5	1.3	-16.7	4.0	-0.83
$S_2$	-22.9	507.2	6.5	-6.2	-0.1	-22.3	19.7	454.9	-1.1	-7.0	20.9	23.0
$S_3$	-242.2	287.9	1.7	-13.3	34.0	1.2	-236.8	-197.5	1.3	16.7	4.0	0.83
$S_4$	265.0	219.3	3.2	-19.5	23.2	0.83	217.1	256.5	3.1	9.7	-8.3	1.2
$S_5$	-22.9	-507.2	6.5	6.2	-0.1	22.3	19.7	-454.9	-1.1	7.0	20.9	-23.0
$S_6$	265.0	-219.3	3.2	19.5	23.2	-0.83	217.2	-256.5	3.1	-9.7	-8.3	-1.2

According to [21] the data [22, 23] were ‘falsely analysed’. We note, however, that the axis system A [20, 21] can be converted into the system B [20, 21] by  $S_5$  followed by  $S_3$ . Hence, for a meaningful comparison of data from different sources [21–23], instead of presenting data in several axis systems as in [21], proper transformations should be carried out adhering to the standard convention  $0 \leq \lambda' \leq 1$ .

**4.2.2.  $\text{Mn}^{2+}$  in  $\text{MnF}_2$  and  $\text{ZnF}_2$ .** The site symmetry for  $\text{Mn}^{2+}$  in  $\text{MnF}_2$  and  $\text{ZnF}_2$  is  $D_{2h}$ ; however the crystal field parameters were calculated using  $D_2$  symmetry [24]. Four non-standard  $D$  and  $E$  sets were reported [24]: (I) theoretically calculated using spin–spin and (II) spin–orbit mechanisms, (III) total values and (IV) the experimental values of [25]. The standard  $b_2^0$  and  $b_2^2$  sets are provided in table 3.

**4.2.3.  $\text{Mn}^0$ :  $\text{BaF}_2$ .** One  $\text{Mn}^+$  centre and two different  $\text{Mn}^0$  ( ${}^6S_{5/2}$ ) centres were observed in  $\text{Mn}:\text{BaF}_2$  [26] after x-irradiation at RT. A non-standard  $D$  and  $E$  set (table 3) was obtained for  $\text{Mn}_I^0$  in the axis system with  $z$ : [100],  $x$ :  $\vartheta = 90^\circ$ ,  $\varphi = 24.6^\circ$ ,  $y$ :  $\vartheta = 90^\circ$ ,  $\varphi = 114.6^\circ$ , whereas a standard set for  $\text{Mn}_{II}^0$ :  $D = 599.3$ ,  $E = 76.3$  with  $z$ :  $\vartheta = 35.5^\circ$ ,  $\varphi = 0^\circ$ ,  $x$ :  $\vartheta = 125.5^\circ$ ,  $\varphi = 0^\circ$ ,  $y$ :  $\vartheta = 125.5^\circ$ ,  $\varphi = 90^\circ$  [26]. The site symmetry was given only for the  $\text{Mn}^+$  centre as  $C_4$  [26]. After standardization the sign of both  $D$  and  $E$  for the  $\text{Mn}_I^0$  centre changes to negative. Since for  $\text{Mn}^0$  the principal axes do not coincide with the symmetry axes, the actual site symmetry is lower than orthorhombic. In the case of several distinct low symmetry centres in a given host it is more meaningful to provide two SH parameter sets for each centre: (i) one expressed in a common symmetry-based axis system, and (ii) one expressed in a local principal axis system with the orientation of the principal axes referred to the common axis system.

**4.2.4.  $\text{Ni}^{2+}$  and  $\text{V}^{2+}$  in  $\text{ZnF}_2$ .** The site symmetry is not defined in [27], whereas the  $z$  ( $x$ ) axis is taken along the [001] ([110]) axis of  $\text{ZnF}_2$ . The experimental non-standard  $D$  and  $E$  [27] and the standardized ones are given in table 3.

**4.2.5.  $\text{Mn}^{2+}$  in  $\text{CaF}_2$ ,  $\text{BaF}_2$  and  $\text{SrF}_2$ .** The SH used for  $\text{Mn}^{2+}$  centres in  $\text{Ca}_{1-x}\text{Ba}_x\text{F}_2$  and  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$  [28–30] involves orthorhombic ZFS parameters  $B_l^m$  associated with conventional combinations of the spin operators:  $S_z$ ,  $S_x$ ,  $S_y$  and  $S_\pm$ , which on inspection turn out to correspond directly to the ES operators  $O_k^q$  [2, 8]. Hence  $B_l^m$  in [28–30] are equivalent to  $B_k^q$  (ES) [2, 8]. Such mixed notations may be easily misinterpreted by others and should

**Table 3.** The original and standardized ZFS parameters, including the errors, for transition-metal ions at orthorhombic sites in AB<sub>2</sub> compounds. For explanation of the sets see text.

Ion: host	Set	OU	Original parameters conventional notation				Standardized ES parameters $b_k^q$ (in $10^{-3} \text{ cm}^{-1}$ )				Ref.
			D	E	E/D	TR	$b_0^0$	$b_2^2$	$b_4^4$	$b_2^2/b_4^4$	
Mn <sup>2+</sup> :MgF <sub>2</sub>	I	$10^{-4} \text{ cm}^{-1}$	$-67.6 \pm 0.2$	$-122 \pm 0.2$	1.81	S <sub>5</sub>	$216.8 \pm 0.3$	$81.6 \pm 0.4$	0.38	[20, 21]	
	II		$-50.0 \pm 6.0$	$-149 \pm 4.0$	2.98	S <sub>5</sub>	$248.5 \pm 6.7$	$148.5 \pm 11$	0.60	[20]	
	III		$-164 \pm 10.0$	$-178 \pm 5.0$	1.09	S <sub>5</sub>	$349.0 \pm 9.0$	$21.0 \pm 17$	0.06	[20]	
Mn <sup>2+</sup> :MnF <sub>2</sub>	I	$10^{-4} \text{ cm}^{-1}$	$-10.5 \pm 2$	$14.0 \pm 2$	-1.33	S <sub>6</sub>	$26.3 \pm 3.2$	$5.3 \pm 4.2$	0.20	[24]	
	II		$44.5 \pm 5$	$-131 \pm 10$	-2.94	S <sub>6</sub>	$-218.8 \pm 15$	$-129.8 \pm 17$	0.59	[24]	
	III		$34.0 \pm 5$	$-117 \pm 10$	-3.44	S <sub>6</sub>	$-193.0 \pm 15$	$124.5 \pm 17$	0.65	[24]	
	IV		$34.5 \pm 5$	$-121.5 \pm 10$	-3.52	S <sub>6</sub>	$-200.0 \pm 15$	$-130.5 \pm 7$	0.65	[25]	
Mn <sup>2+</sup> :ZnF <sub>2</sub>	I	$10^{-4} \text{ cm}^{-1}$	$-6.6 \pm 2$	$11.0 \pm 2$	-1.67	S <sub>6</sub>	$19.8 \pm 3.2$	$6.6 \pm 4.2$	0.33	[24]	
	II		$39.4 \pm 5$	$-131.1 \pm 10$	-3.33	S <sub>6</sub>	$-216.2 \pm 15$	$-137.4 \pm 17$	0.64	[24]	
	III		$32.8 \pm 5$	$-120 \pm 10$	-3.66	S <sub>6</sub>	$-196.4 \pm 15$	$-130.8 \pm 17$	0.67	[24]	
	IV		$31.5 \pm 5$	$-113.5 \pm 10$	-3.60	S <sub>6</sub>	$-186 \pm 15$	$-123 \pm 17$	0.66	[25]	
Mn:BaF <sub>2</sub>	Mn <sub>J</sub> <sup>0</sup>	$10^{-4} \text{ cm}^{-1}$	430.6	243.3	0.57	S <sub>2</sub>	-580.3	-280.9	0.48	[26]	
Ni <sup>2+</sup> :ZnF <sub>2</sub>		GHz	125.5	80.1	0.64	S <sub>2</sub>	-61008	-22715	0.38	[27]	
V <sup>2+</sup> :ZnF <sub>2</sub>		GHz	12.74	4.58	0.36	S <sub>2</sub>	-4416.3	-4082.8	0.93	[27]	



be replaced by a well defined tensor-operator notation [2, 8]. In table 4, RT denotes the experimental room temperature values and PPI denotes the theoretical values calculated using the polarizable point ion (PPI) model [28, 29]. The maximum splitting of the spectrum was observed [28, 29] along the [110]-direction taken as the  $z$ -axis and with  $x_{\parallel}$ [110] and  $y_{\parallel}$ [ $\bar{1}\bar{1}0$ ]. No explicit definition of the axis system was provided in [30]. An alternative assignment of the EPR transitions was also used in [28–30], resulting in standard sets given in table 4 for comparison.

Note that the ZFS parameters  $B_k^q$  were referred to as the ‘*crystal field*’ ones [30]. Closer examination of the PPI model [28–30] reveals that it originates from papers [31–33] and confuses the CF Hamiltonian and ZFS Hamiltonian. Various degrees of this confusion have been identified in [2]. Point charge (or equivalent) models are applicable only to CF parameters (so with very poor results), since they are directly related to the electric field of ligands, and should not be used for ZFS parameters [2]. Since the PPI model [28, 29, 31–33] uses ‘adjustable’ parameters, in spite of its inapplicability, ZFS parameters can be fitted in a semi-empirical way. The superposition model [34, 35] also used in [28, 29] can be applied both to ZFS parameters and CF ones. For each Hamiltonian  $\mathcal{H}_{CF}$  and  $\mathcal{H}_{ZFS}$  a *different* set of the adjustable superposition model parameters, i.e. the intrinsic parameters  $\bar{B}_k(R_0)$  and the power law exponents  $t_k$ , is derived in a semi-empirical way from the optical and EPR spectra for  $\mathcal{H}_{CF}$  and  $\mathcal{H}_{ZFS}$ , respectively. Therefore, not much physical significance can be attached to the values  $B_k^q$  (PPI) [28, 29] (table 4). The statement [29] that ‘the SH parameters in table 1 are a good choice rather than those in table 2’ is not conclusive since it is based on the experimental non-standard  $B_2^2/B_2^0$  [29], which can always be limited to the standard range. Note that the SH parameter sets transformed by any  $S_i$ , so numerically different (as e.g. in table 2), are physically equivalent.

#### 4.3. $ABO_4$ compounds

**4.3.1.  $VO_4^{3-}$  in  $YVO_4$  and  $YP_{0.96}V_{0.04}O_4$ .** The non-standard  $|D|$  and  $|E|$  sets (table I of [36]) for  $VO_4^{3-}$  in  $YVO_4$  (I–IV) and  $YP_{0.96}V_{0.04}O_4$  (V–VIII) from experiments in magnetic field (I–III and V–VII) and in zero field (IV and VIII) are standardized (table 5). The axes were defined [36]: the  $z$ -axis  $\parallel$  V–O bond and  $y \perp ac$  or  $bc$  crystallographic plane. The  $VO_4^{3-}$  site symmetry, assumed in [36] as tetragonal  $D_{2d}$ , must be actually lower than orthorhombic since the principal axes of the  $\mathbf{D}$  tensor are different from those of the  $\mathbf{g}$  matrix. The set IV [36]:  $|D| = 0.58$  and  $|E| = 13.72$  (GHz), is obtained from the earlier zero-field EPR data [37]:  $|D| = 20.25$  and  $|E| = 7.15$  (GHz), by the interchange  $(x, y, z)$  [37] to  $(y, z, x)$  [36]. This is actually the transformation  $S_5$ , which yields  $D = -20.85$  and  $E = 6.55$  (GHz). It appears that the set IV [36] was obtained from the data [37] by the transformation  $S_6$ , which yields:  $D = 0.60$  and  $E = 13.7$  (GHz), differing slightly from the set IV [36]; this may be due to rounding of the values.

**4.3.2.  $MoO_4^{2-}$  in  $CaMoO_4$ .** Similarly to [36], for  $MoO_4^{2-}$ : $CaMoO_4$  [38] four  $D$  and  $E$  sets were obtained from experiments in magnetic field (I–III) and in zero field (IV) (table 5). The  $\mathbf{D}$ -tensor principal axes determined from EPR spectra are referred to the crystallographic  $a$ ,  $b$ ,  $c$  directions in the unit cell of  $CaMoO_4$ . The conclusion [38]: ‘The directions of the principal axes of the ZFS tensor indicate that the  $MoO_4^{2-}$  ion, having  $D_{2d}$  ground state symmetry, is distorted to an approximate  $C_{3v}$  symmetry on excitation’, should be revised since the spectra [38] indicate a site symmetry lower than orthorhombic.

**Table 4.** The original and standardized ZFS parameters, including the errors, for transition-metal ions at orthorhombic sites in AB<sub>2</sub> compounds. For explanation of the sets see text. The value of  $g = 2.001$  for all hosts [28–30] is used for original unit conversion.

Centre:host Set	OU	Original ES parameters $B_k^q$						Standardized ES parameters $b_k^q$ (in $10^{-4} \text{ cm}^{-1}$ )						Ref.	
		$B_2^0$	$B_2^2$	$B_4^0$	$B_4^2$	$B_4^4$	$B_2^0/B_2^2$	TR	$b_2^0$	$b_2^2$	$b_4^0$	$b_4^2$	$b_4^4$		$b_2^0/b_2^2$
Mn <sup>2+</sup> -Ba <sup>2+</sup> :CaF <sub>2</sub> RT PPI	Gauss	-20.59	-63.01	-0.022	-0.016	0.028	3.06	S <sub>5</sub>	117.2	1.74	-0.38	4.32	-4.41	0.02	[28]
		-12.58	-45.34	—	—	—	3.06	S <sub>5</sub>	81.04	10.52	—	—	—	0.13	[28]
Mn <sup>2+</sup> -Sr <sup>2+</sup> :CaF <sub>2</sub> RT PPI	Gauss	-10.39	-26.83	0.005	-0.022	-0.058	-2.58	S <sub>2</sub>	52.16	6.08	-0.46	1.71	1.90	0.12	[28, 29]
		-7.38	-22.20	—	—	—	3.01	S <sub>5</sub>	41.45	0.08	—	—	—	0.002	[28]
Mn <sup>2+</sup> -Ba <sup>2+</sup> :SrF <sub>2</sub> RT	Gauss	-18.29	-45.02	0.016	-0.042	-0.058	2.46	S <sub>2</sub>	88.71	13.80	-0.36	2.69	5.58	0.16	[29]
Mn <sup>2+</sup> -Sr <sup>2+</sup> :CaF <sub>2</sub> RT	Gauss	-18.12	-1.77	-0.003	0.026	-0.061	0.098	S <sub>1</sub>	-50.78	-4.96	-0.17	-1.46	-3.4	0.098	[29]
		18.12	1.77	0.003	-0.026	0.0608	0.098	S <sub>1</sub>	50.78	4.96	0.17	-1.46	3.4	0.098	[30]
Mn <sup>2+</sup> -Ba <sup>2+</sup> :SrF <sub>2</sub> <sup>a</sup> RT	Gauss	-31.66	4.93	0.006	-0.049	-0.099	0.16	S <sub>1</sub>	-88.73	13.82	-0.34	-2.75	-5.55	0.16	[29]

<sup>a</sup>The original standard values listed here for comparison (see text).

**Table 5.** The original and standardized ZFS parameters, including the errors, for transition-metal ions at orthorhombic sites in  $ABO_4$  compounds. For explanation of the sets see text.

Ion: host	Set	OU	Original parameters				Standardized ES parameters $b_k^q$				Ref.
			D	E	E/D	TR	$b_2^0$	$b_2^2$	$b_2^2/b_2^0$	(in $10^{-3} \text{ cm}^{-1}$ )	
$VO_4^{3-}$ :YVO <sub>4</sub>	I	GHz	$0.529 \pm 0.035$	$13.712 \pm 0.022$	25.92	S <sub>5</sub>	$-6949 \pm 12$	$-6596 \pm 21$	0.95	[36]	
	II		$0.534 \pm 0.035$	$13.709 \pm 0.022$	25.67		$-6948 \pm 12$	$-6592 \pm 21$	0.95	[36]	
	III		$0.519 \pm 0.037$	$13.730 \pm 0.023$	26.45		$-6956 \pm 13$	$-6610 \pm 22$	0.95	[36]	
	IV		$0.58 \pm 0.04$	$13.72 \pm 0.04$	23.65		$-6961 \pm 21$	$-6575 \pm 28$	0.94	[37]	
$VO_4^{3-}$ :Y <sub>0.96</sub> P <sub>0.04</sub> O <sub>4</sub>	V	GHz	$1.159 \pm 0.045$	$12.863 \pm 0.030$	11.10	S <sub>5</sub>	$-6629 \pm 17$	$-5856 \pm 27$	0.88	[36]	
	VI		$1.158 \pm 0.046$	$12.861 \pm 0.030$	11.11		$-6628 \pm 17$	$-5855 \pm 27$	0.88	[36]	
	VII		$1.183 \pm 0.048$	$12.870 \pm 0.031$	10.88		$-6637 \pm 18$	$-5847 \pm 29$	0.88	[36]	
	VIII		$1.12 \pm 0.04$	$12.98 \pm 0.04$	11.59		$-6681 \pm 21$	$-5934 \pm 28$	0.89	[37]	
$MoO_4^{2-}$ :CaMoO <sub>4</sub>	I	MHz	$-94.270 \pm 70$	$32.680 \pm 30$	0.35	S <sub>4</sub>	$32.073 \pm 19$	$30.816 \pm 38$	0.96	[38]	
	II		$-94.290 \pm 70$	$32.675 \pm 30$	0.35		$32.074 \pm 19$	$30.829 \pm 38$	0.96	[38]	
	III		$-94.265 \pm 75$	$32.675 \pm 30$	0.35		$32.074 \pm 19$	$30.829 \pm 38$	0.96	[38]	
	IV		$-94.358 \pm 20$	$32.697 \pm 20$	0.35		$32.097 \pm 11$	$30.852 \pm 14$	0.96	[38]	

#### 4.4. Miscellaneous compounds

4.4.1.  $Fe^{3+}$ : tremolite. The non-standard  $D$  and  $E$  for  $Fe^{3+}$  in tremolite [39] are standardized (table 6). No site symmetry or definition of the axis system is given [39]. The original fourth-order ZFS parameters:  $a = 0.0026$  and  $F = 0.040$  ( $cm^{-1}$ ) yield the standardized ones  $b_4^q$  (ES):  $b_4^0 = 6.3$ ,  $b_4^2 = 33.3$  and  $b_4^4 = 64.9$  ( $10^{-4} cm^{-1}$ ). The sign of  $D$  and  $E$  has changed from positive to negative after the transformation  $S_2$ .

4.4.2.  $Mn^{2+}$ :  $NaNO_2$ . Theoretically calculated [40]  $D$  and  $E$  for  $Mn^{2+}$  at the N site are unusually high as compared with those at the Na site (table 6). The point charge model yields the set I ( $N = 0.942$ ) and II ( $N = 0.956$ ), whereas the superposition model yields the set III ( $N = 0.942$ ) and IV ( $N = 0.956$ ), where  $N$  is the average covalency parameter. Only the sign of  $E/D$  is considered [40]. Note that in [40] both the point charge model and superposition model are applied first to deduce CF parameters, which are then used in the microscopic SH expressions for  $D$  and  $E$  due to the spin-orbit mechanism [40]. Hence it is a correct procedure unlike the application of the PPI model [28, 29, 31–33] discussed in section 4.2.5.

4.4.3.  $Mn^{2+}$ :  $C_4H_6MgO_4 \cdot 2H_2O$  (MMDH) and  $C_4H_4MgO_5 \cdot 5H_2O$  (MMPH). A truncated orthorhombic SH with  $D$ ,  $E$  (table 6) and  $a$  only was used for  $Mn^{2+}$  in magnesium maleate dihydrate (MMDH) [41] and pentahydrate (MMPH) [42]. No site symmetry or definition of the axis system is given [41, 42]. The values of  $a$  [41, 42] are not reliable since the parameters  $F$  and  $K$  [2] were neglected. For  $Mn^{2+}$ :MMDH,  $a = 1.5$  Gauss [41] yields the standardized:  $b_4^0 = 0.71$ ,  $b_4^2 \equiv 0$  and  $b_4^4 = 3.55$  ( $10^{-4} cm^{-1}$ ). Similarly for  $Mn^{2+}$ :MMPH,  $a = 16$  Gauss [42] yields:  $b_4^0 = 7.59$ ,  $b_4^2 \equiv 0$  and  $b_4^4 = 38.0$  ( $10^{-4} cm^{-1}$ ). The non-standard SH parameters for  $Mn^{2+}$  in MMDH [41] and MMPH [42] were directly compared with those for  $Mn^{2+}$  ions doped in different carboxylic salts in spite of different conventions being used [41, 42]. For  $Mn^{2+}$ :MMPH another set at 120 K:  $D = 240.0$ ,  $E = 78.0$  ( $E/D = 0.32$ ), and  $a = 19$  (Gauss) was obtained [42]. This temperature dependence of SH parameters suggests a possible structural phase transition between 300 K and 120 K.

4.4.4.  $Mn^{2+}$  and  $Fe^{3+}$  in  $XS_2Se_2$ . Orthorhombic defect centres:  $Mn^{2+}$  in an  $MnS_2Se_2$  cluster and  $Fe^{3+}$  in an  $FeS_2Se_2$  cluster in ZnS/ZnSe mixed crystals [43] yield  $D$  and  $E$ , which after standardization are not comparable with  $|D|$  and  $|E|$  for  $Mn^{2+}$  ions in other hosts [44]. Hence  $D$  and  $E$  [43] were either given in inappropriate units or inaccurately extracted from EPR spectra. The conclusion [43] from ‘the  $FeS_2Se_2$  cluster has  $C_{2v}$  symmetry’ that ‘this can account for the large  $E$ . A small  $D$  arises from the fact that the  $Fe^{3+}$  ion can be displaced from the centre position of the ideal tetrahedron towards the pair of  $S^{2-}$  or  $Se^{2-}$  ions’ is inaccurate, since the relation  $E \gg D$  cannot imply a very large rhombic distortion (see section 3).

4.4.5.  $Cr^{3+}$  in  $(DMA)_2SnCl_6$ . EPR spectra of thermally produced Cr(III) species in  $[(CH_3)_2NH_2]_2SnCl_6$  [45] were fitted with non-standard  $D$  and  $E$ , and isotropic  $g = 1.986$  (table 6). The local site symmetry at the Sn position is monoclinic ( $m/C_{1h}$ ) [45]. From EPR spectra, the  $a$ -axis was ‘observed as a principal axis for the ligand field actually ZFS term in SH, and the other two principal axes were found to lie on the  $bc$  plane’. Hence, the orthorhombic SH [45] is only an approximation and the low symmetry effects may be significant. The closeness (table 6) of the non-standard [45] and standardized ratio  $|E/D|$  to 0.333, or  $|b_2^0/b_2^2|$  to 1, indicates that the distortion of the Cr(III) complex is close to the maximum limit.

**Table 6.** The original and standardized ZFS parameters, including the errors, for transition-metal ions at orthorhombic sites in ABO<sub>4</sub> compounds. For explanation of the sets see text.

Ion: host	Set	OU	Original parameters Conventional notation			Standardized ES parameters $b_k^g$ (in $10^{-3} \text{ cm}^{-1}$ )				Ref.
			D	E	E/D	TR	$b_2^0$	$b_2^g$	$b_2^0/b_2^g$	
Fe <sup>3+</sup> : tremolite		cm <sup>-1</sup>	1.0294	0.3738	0.36	S <sub>2</sub>	-1075.4	-983.4	0.91	[39]
Mn <sup>2+</sup> : NaNO <sub>2</sub> (N site)	I	10 <sup>-4</sup> cm <sup>-1</sup>	15 113	17 202	1.14	S <sub>5</sub>	-33 360	-31 333.5	0.09	[40]
	II		14 144	16 037	1.13		-2839.5		0.09	
	III		43 188	133 514	3.09		-221 870	-135 490	0.61	
	IV		40 278	124 317	3.09		-206 610	-126 060	0.61	
Mn <sup>2+</sup> : MMDH	300 K	Gauss <sup>a</sup>	353	172	0.49	S <sub>2</sub>	-411.7	-257.3	0.62	[41]
Mn <sup>2+</sup> : MIMPH	300 K	Gauss <sup>b</sup>	207	110	0.53	S <sub>2</sub>	-254.7	-138.0	0.54	[42]
Mn <sup>2+</sup> : MnS <sub>2</sub> Se <sub>2</sub>		10 <sup>-4</sup> cm <sup>-1</sup>	80 ± 20	780 ± 50	9.75	S <sub>5</sub>	-1210 ± 75.6	-1050 ± 80.8	0.87	[43]
Fe <sup>3+</sup> : MnS <sub>2</sub> Se <sub>2</sub>		10 <sup>-4</sup> cm <sup>-1</sup>	10 000 ± 2 000	1000 ± 300	10.0	S <sub>5</sub>	-15 500 ± 3 004	-13 500 ± 3 034	0.87	[43]
Cr <sup>3+</sup> : [DMA] <sub>2</sub> SnCl <sub>6</sub>		Gauss <sup>c</sup>	767	-293	-0.38	S <sub>4</sub>	-763.07	-659.22	0.86	[45]
ES notation $B_k^g$										
			$B_2^0$	$B_2^g$	$B_2^g/B_2^0$					
Phenanthrene		10 <sup>-4</sup> cm <sup>-1</sup>	353 ± 5	-484 ± 5	-1.37	S <sub>4</sub>	-1254 ± 10.6	-864 ± 23.7	0.69	[46]
Mn <sup>2+</sup> : Sn <sub>2</sub> P <sub>2</sub> S <sub>6</sub>		10 <sup>-4</sup> cm <sup>-1</sup>	110 ± 3	139 ± 3	1.26	S <sub>2</sub>	-373.5 ± 6.4	-286.5 ± 14.2	0.77	[48]

<sup>a-c</sup> The value of the *g*-factor given in the original reference: 2.030, 2.032 and 1.986, respectively, is used for unit conversion.

4.4.6. *Phenanthrene*. For the triplet ( $S = 1$ ) state in phenanthrene  $b_2^0$  and  $b_2^2$  [46, 47] obtained in the biphenyl molecular axis system (table 1 of [46]) after standardization (table 6) are comparable, apart from the sign of  $b_2^0$ , with  $b_2^0 = 1020$  and  $b_2^2 = -450$  ( $10^{-4} \text{ cm}^{-1}$ ) for naphthalene [47].

4.4.7. *Mn<sup>2+</sup> in Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>*. Two different  $B_k^q$  (ES) sets were reported for Mn<sup>2+</sup> in Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> [48]: a standard set at 300 K, i.e.  $b_k^q$  (ES):  $b_2^0 = 489$  and  $b_2^2 = 477$  ( $10^{-4} \text{ cm}^{-1}$ ), and a non-standard set at 330 K (table 6).

## 5. Conclusions

A literature survey has revealed a great deal of diversity of notations, units and conventions for the axis systems used in EPR studies of transition ions at orthorhombic sites in various crystals. Hence a direct comparison of spin-Hamiltonian parameters can only be achieved after proper conversions and/or transformations. The CST package [1] has been developed and used for this purpose. The results of the analysis and standardization of orthorhombic ZFS parameters for transition-metal centres carried out in this paper highlight three points. First, they exemplify the difficulties faced during development of a computerized database of ZFS parameters. Second, they indicate the urgent need for internationally accepted guidelines for unified presentation of ZFS parameters. Third, they show the benefits of unified data presentation, which enables not only direct comparison of data but also an identification of inconsistencies in various data sets. Importantly, we have also clarified the question concerning structural implications of the large ratio of  $E/D$  or  $B_2^2/B_2^0 = b_2^2/b_2^0$ .

In view of these results we suggest adopting the following guidelines for presentation of ZFS parameters: (i) the extended Stevens operators and the parameters  $b_k^q$  as the standard notation, (ii) units of  $10^{-4} \text{ cm}^{-1}$  and (iii) the axis system conforming to the standard range of the ratio  $0 \leq \lambda' \equiv b_2^2/b_2^0 \leq 1$  for orthorhombic symmetry. It is worth noting that the guidelines (i) and partially (ii) have been adopted, e.g. in the reviews dealing with EPR data for Mn<sup>2+</sup> [44, 49, 50], and Fe<sup>3+</sup> and Cr<sup>3+</sup> in minerals [51]. The conventional  $D$  and  $E$  (in  $\text{cm}^{-1}$ ) were reported for Cr<sup>3+</sup> in single crystals [52]. On the other hand the reviews published in the *Specialist Periodical Reports on ESR* (see, e.g. [53–55]) provide only a general description of EPR related literature without reporting the SH parameter values. In the *Magnetic Resonance Reviews* series, see e.g. [56–58], reporting of the original parameters and units has been adopted. In view of the variety of notations, when quoting the reported values from [56–58] care must be taken to verify whether there is no misinterpretation of the original meaning of ZFS parameter symbols. The guideline (iii), which is specific for orthorhombic EPR centres, has been mentioned in several reviews, e.g. dealing with EPR of co-ordination and organometallic transition metal compounds [59], iron containing proteins [60, 61], ESR in glasses [62] and EPR in mineralogy [63]. Implementation of the above guidelines requires conversion and standardization of the original data, which can efficiently be carried out using the CST package [1].

Finally, support for the guidelines, especially the first one, from a pioneer in the EPR area is noted [64]: ‘The reader is therefore advised to consult the papers by C Rudowicz, particularly, [references [8], [9] and [2] in the present article] for a critical account of the current literature and for proposals for future standardization in the definitions and notations. A step forward would seem to be to adopt his suggestions’.

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