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Alternative zero-field splitting (ZFS) parameter sets and standardization for Mn^{2+} ions in various hosts exhibiting orthorhombic site symmetry

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Abstract

The intrinsic properties of orthorhombic Hamiltonians, e.g. zero-field splitting (ZFS) ones or crystal-field (CF) ones, embodied in the standardization idea may be utilized to improve reliability and comparability of experimentally determined ZFS (or CF) parameters. These properties have enabled derivation of transformation relations for Hamiltonian parameters expressed in several related axis systems defined earlier by one of us. In this paper the standardization transformations are used to generate alternative physically equivalent yet numerically distinct parameter sets for Mn^{2+} ions in various hosts exhibiting orthorhombic or lower site symmetry. One parameter set out of six alternative sets satisfies the standardization criteria. Importantly, the standardized sets should be used for direct comparisons. Several non-standard ZFS parameter (ZFSP) sets for Mn^{2+} ions in crystals, identified in our literature survey of EMR studies, are here standardized. Thus the ratio of $\lambda = E/D$ or $\lambda' = B_2^2/B_2^0$ is limited to the standard range $(0, \pm 1/3)$ or $(0, \pm 1)$, respectively. Our considerations provide useful correlations between the distinct and non-compatible yet physically equivalent ZFS parameter sets reported in literature. All calculated alternative sets are tabularized for ten Mn^{2+} complexes considered. These ZFSP sets may serve for application of the multiple correlated fitting techniques in follow-up EMR studies. Some misinterpretations yielding ambiguous and unreliable results are clarified. The intricate low symmetry aspects are also discussed, whenever applicable. The results of this paper enable more reliable analysis, comparison, and fitting of ZFSP sets from EMR spectra for Mn^{2+} ions in various crystals.

Keywords: A. Inorganic compounds; optical materials; D. Defects; D. Electron paramagnetic resonance (EPR)

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1. Introduction

The concept underlying EMR (electron magnetic resonance, which encompasses EPR/ESR (electron paramagnetic/spin resonance) spectroscopy [1, 2] is the spin Hamiltonian (SH) - for a review, see, e.g. Refs 3, 4. Two major terms in SH are the electronic Zeeman Hamiltonian and the zero-field splitting (ZFS) one. The latter Hamiltonian is often confused in EMR literature with the crystal-field (CF) Hamiltonian, in spite of their physically different nature [5]. The standardization idea has originally been introduced in EMR area for the second-rank conventional ZFS terms based on the observation that the ratio of the orthorhombic (E) to axial (D) ZFS parameters (ZFSPs): $\lambda = E/D$ can always be limited to the range $(0, \pm 1/3)$ by appropriate choice of coordinate system [6, 7, 8]. Based on this idea two standardization conventions have been proposed [9,10]. The standard range $0 \leq \lambda \leq 1/3$ corresponds [9] in terms of the diagonal components of the conventional ZFS $\mathbf{D}$ tensor ($\mathbf{S.D.S}$) [11,12] to $|D_{xx}| \leq |D_{yy}| \leq |D_{zz}|$, whereas $-1/3 \leq \lambda \leq 0$ corresponds [10] to $|D_{yy}| < |D_{xx}| \leq |D_{zz}|$. Hence, the former (later) convention is equivalent to choosing the direction of the maximum overall splitting of an EPR spectrum as the Z axis and that

of the minimum as the X axis (Y axis) [13, 14, 15, 16]. The convention $0 \leq \lambda \leq 1/3$ is mostly used in EMR studies of transition-metal ions [17]. Interestingly, an alternative ordering condition: $|D_{YY}| \geq |D_{XX}| \geq |D_{ZZ}|$ has been proposed [18], which supposedly describes better the ‘extreme rhombic distortion’, i.e. the maximum rhombicity. Judging by the Science Citation Index search, it appears that the latter convention has not become adopted in EMR literature.

Using the transformation properties of the extended Stevens operators [19] the standardization idea has been generalized to the fourth- and six-rank orthorhombic [20] and monoclinic [21] ZFS as well as CF terms. Since the mid-1980 the standardization idea have also spread out into optical spectroscopy area and the number of pertinent applications for the orthorhombic CF parameters is growing steadily (for references, see, e.g., the recent papers [22, 23, 24]).

The organization of this paper is as follows. In Section 2 we briefly recall the theoretical aspects underlying the orthorhombic standardization. In Section 3 applications to several non-standard ZFS parameter sets identified in our literature survey of EMR studies for Mn^{2+} ions in various hosts exhibiting orthorhombic site symmetry are considered. Calculations are facilitated by the package CST for conversions, standardization, and transformations of ZFS (or CF) parameters [25, 26]. Conclusions are presented in Section 4.

2. Basic Nomenclature and Theoretical Aspects

The usual Stevens operators [1, 2] O_k^q (O_n^m), with the positive q components only, have dominantly been used in EMR studies [27, 28] and to a lesser extend in the crystal field theory and superposition model analysis [29, 30, 31]. Group theory predicts that for lower symmetry cases the negative q components are required [2, 3, 4]. For this purpose, the extended Stevens (ES) operators, which include both the positive and negative q components, have been defined and their transformation properties worked out [19]. Note that the ES operators $O_k^q(X)$ have recently been generalized to any rank k and quantum number X of the angular momentum operator $X = S, J$, or L [32].

For arbitrary low, i.e. triclinic, site symmetry the spin Hamiltonian, including the Zeeman electronic (Ze) terms and ZFS ones in the ES operators notation [3, 19, 32], is defined by [1-5]:

$$H_{\text{spin}} = H_{\text{Ze}} + H_{\text{ZFS}} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_{k=2,4,6} \sum_{q=-k}^k B_k^q O_k^q(S_X, S_Y, S_Z). \quad (1)$$

Transformations between the g_{ij} –factors and ZFS parameters expressed in different axis systems (X, Y, Z) have been provided in Ref. 33. Often the “scaled” b_k^q parameters [1-5] are used in literature:

$$b_2^q = 3 B_2^q, \quad b_4^q = 60 B_4^q, \quad b_6^q = 1260 B_6^q. \quad (2)$$

The following relations between the conventional orthorhombic ZFSPs and those in Eq. (1) and (2) hold [1, 3-5]:

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

Readers should be warned about the incorrect relations between the ZFSPs in the ES notation and conventional one (**S.D.S**) for orthorhombic and lower symmetry that have appeared in EMR literature as clarified in Ref. 34.

Importantly, the ligand (crystal) field Hamiltonian H_{CF} can be expressed in mathematically same form as H_{ZFS} in Eq. (1) upon replacement of the spin operator $\mathbf{S}$ by the angular momentum $\mathbf{L}$ or $\mathbf{J}$ [1-5]. Therefore, the standardization idea can also be applied to an orthorhombic H_{CF} . Our survey shows that various axis systems have

been used in an arbitrary way in literature. The equivalence of orthorhombic CF parameter sets expressed in several related axis systems have been partially recognized as early as in 1976 [35]. In the review [36] partial transformation relations for the CF parameters B_{kq} (in tensor notation) have been given but the parameters have arbitrarily been converted.

The rhombicity ratio $\lambda \equiv E/D$ or alternatively $\lambda' \equiv B_2^2/B_2^0 \equiv b_2^2/b_2^0$ plays an important role in description of the intrinsic features of ZFS (CF) Hamiltonians for orthorhombic or lower symmetry [20, 21]. For readers' convenience, we briefly recap here the major aspects. For details the papers [20-24] may be consulted. There exist three mutually perpendicular and equivalent symmetry axes for orthorhombic symmetry groups (C_{2v} , D_2 , and D_{2h}) [37,38]. The various choices of the axes (X, Y, Z) for the operators O_k^q in Eq. (1) with respect to the crystallographic axis system (CAS) or symmetry-adapted axis system (SAAS) [39] result in different sets of B_k^q parameters. The operators and parameters in an original axis system are denoted by curly brackets and those in the transformed axis systems by square brackets. From fitting EMR spectra an experimental ratio $\{\lambda\}$ or $\{\lambda'\}$ may be obtained, in general, of any value in the range $(-\infty, +\infty)$. On transforming to a proper axis system the ratio $[\lambda]$ and $[\lambda']$ may be confined to the standard range $(0, \pm 1/3)$ and $(0, 1)$, respectively. For this purpose, six related axis systems were chosen [20] as shown in Fig. 1. For illustration, for $k = 2$ the transformed $[B_k^q]$'s in terms of the original $\{B_k^q\}$'s are provided in Table 1 (supplemented by the g_{ij} components). Transformation relations for $k = 4$ and 6 may be found in [20] and [21] for orthorhombic and monoclinic symmetry, respectively.

Note that CF or ZFS parameters determined experimentally using non-directional techniques (e.g. optical spectroscopy or zero-field resonance) may only be assigned a *nominal* axis system, since no specific axis system can be determined from fitting the experimental and theoretical energy levels in such cases [39]. Correlation of the axis systems assigned to experimentally determined ZFSP sets may be possible by comparison with model calculations using, e.g. superposition model analysis [29-31], which must be carried out in a well-defined axis system, usually the crystallographic one.

Table1

Conversion relations [20] for standardization of the orthorhombic second-rank H_{ZFS} (H_{CF}) terms yielding the ratio $[\lambda'] = [B_2^2] / [B_2^0]$ for the transformed parameters within the standard range $(0, 1)$ and the corresponding g -tensor components.

Range of original $\{\lambda'\}$	$(-\infty, -3)$	$(-3, -1)$	$(-1, 0)$	$(1, 3)$	$(3, +\infty)$
Transformation Required	S6	S4	S3	S2	S5
$[B_2^2]$	$\frac{1}{2} (\{B_2^2\} + 3\{B_2^0\})$	$-\frac{1}{2} (\{B_2^2\} + 3\{B_2^0\})$	$-\{B_2^2\}$	$\frac{1}{2} (\{B_2^2\} - 3\{B_2^0\})$	$-\frac{1}{2} (\{B_2^2\} - 3\{B_2^0\})$
$[B_2^0]$	$\frac{1}{2} (\{B_2^2\} - \{B_2^0\})$	$\frac{1}{2} (\{B_2^2\} - \{B_2^0\})$	$\{B_2^0\}$	$-\frac{1}{2} (\{B_2^2\} + \{B_2^0\})$	$-\frac{1}{2} (\{B_2^2\} + \{B_2^0\})$
$[g_x]$	$\{g_z\}$	$\{g_y\}$	$\{g_y\}$	$\{g_x\}$	$\{g_z\}$
$[g_y]$	$\{g_y\}$	$\{g_z\}$	$\{g_x\}$	$\{g_z\}$	$\{g_x\}$
$[g_z]$	$\{g_x\}$	$\{g_x\}$	$\{g_z\}$	$\{g_y\}$	$\{g_y\}$

Fig.1. Definition of the axis systems used for standardization [20] with respect to the original *nominal* [39] system denoted S1 (adapted from [20]).

Two special cases in the mapping of arbitrary $\{B_k^q\}$'s into the “standardized” parameters $[B_k^q]$'s with $[\lambda'] \in (0, 1)$ may be considered [40, 41]. The points $\{\lambda'\} = -3$ and $+3$ are mapped onto the point $[\lambda'] = 0$ via transformation to S4 (or S6) and S2 (or S5), respectively. This represents a “purely” axial case since $[B_2^2] = 0$. Thus $\{B_2^2\} \neq 0$ describes not an *actual* rhombic distortion but an *apparent* one arising from a specific choice of the original axis system. The points $\{\lambda'\} = -\infty$ and $+\infty$ are mapped onto the point $[\lambda'] = 1$ via transformation to S6 and S5, respectively. This represents what is known in literature as the “*fully rhombic*” case (see, e.g. Refs [8, 42, 43, 44]) since $[B_2^2] = [B_2^0] = \pm 1/2 \{B_2^2\}$. Other intricacies concerning the orthorhombic standardization of the second-rank ZFS (CF) terms, especially the sign relationships and number of equivalent solutions, have recently been recognized and discussed [45]. The number of applications of the standardization idea [6-10] has been growing since its comprehensive extensions appeared [20, 21]; see the recent papers [22-24] and references therein. However, as our ongoing survey in Section 3 indicates, some authors are still unaware of this idea and its advantages.

3. Applications

In this section we consider several examples of application of the standardization idea to the orthorhombic 2nd-rank ZFS parameters for Mn^{2+} ions in various hosts exhibiting orthorhombic site symmetry. These examples have been selected to provide a mixture of the early and recent papers to illustrate the problem in historical context across the decades. For each host system brief comments are provided and, whenever applicable, the intricate low symmetry aspects are also discussed. A general comment is pertinent for the magnitude and sign of D , which provides information regarding the local axial symmetry at the transition-metal ion site. The positive value of D is associated with tetragonal compression or trigonal elongation [46, 47].

The alternative sets, calculated using the package CST [25, 26], may serve for application of the multiple correlated fitting technique [21, 39] in follow-up EMR studies. All alternative sets are physically equivalent and yield identical values of energy levels. Independent fittings starting from various areas of parameter space, to which each alternative set belongs, may improve reliability of final fitted ZFSPs. It may be expected that the multiple correlated fitting technique will become more often used in the EMR and optical spectroscopy area. A recent application of this technique to improve reliability of final fitted ZFS parameters has recently appeared [48].

As a reference notation for the ZFS parameters we adopt here B_k^q and units of $[10^{-4} \text{ cm}^{-1}]$ following the recommendations for unification of notations and guidelines for data presentation in EMR area [3, 4, 49]. The appropriately converted and then transformed ZFSP sets together with the original ZFSP values and units (for verification) are listed in Table 2. For the cases where only one or two 4th-rank ZFSPs (i.e. a and/ or F) have been determined there is no point in using standardization for the 4th-rank ZFSPs. The standardized ZFSP sets in Table 2 (indicated in bold) correspond to the values of $|\lambda'|$ below 1. Hence the standardization transformations (S2/S5 or S4/S6) that yield the standardized ZFSP sets can also be easily identified. It appears that the original fittings have been done most probably starting from different areas of the parameter space or the non-standard ZFSP sets were generated by chance by the computer programs used.

$Mn^{2+}: K_2SO_4$

Chowdari et al. [50] measured three spectra for this system, denoted I, II, and III. The analysis was done using only D , E , and a . For the magnetic field $\mathbf{H} \parallel$ the Z -axis (taken as the site-symmetry axis) only one set of five sextets was observed (spectrum I) and was assigned as due to the first neighbour β - β complex. The spectrum II was due to Mn^{2+} associated with the second neighbour β - K^+ vacancies with the local symmetry axis of this complex making an angle 38° with the crystallographic $\mathbf{b}$ axis. The spectrum III was due to Mn^{2+} substituting β - K^+ site and associated with the third neighbour β - K^+ vacancies with the local symmetry axis making an angle of 22° with the crystallographic $\mathbf{b}$ axis. Standardization transformation is S4/S6. Thus the local axes in which the ZFSPs in Table I of [50] were expressed vary for the three spectra. Hence, these ZFSP values have the meaning of approximate experimentally determined principal values of the tensor $\mathbf{D}$. For full comparison it would be necessary to back transform the experimental D and E to a common axis system as proposed in the recent analysis [51] of EMR spectra for Fe^{3+} in hexagonal $BaTiO_3$ [52, 53]. Since the nearby vacancies were necessary for charge compensation, the actual site symmetry must be lower than that for the undistorted host. Moreover, for various possible locations of the vacancies, various magnetically inequivalent sites may appear with different orientation w.r.t. the original CAS.

$Mn^{2+}: Mg(H_2O)_6H_2EDTA$

Narayana et al. [54] used only the 2nd-rank axial (D) and rhombic (E) ZFS parameters and the isotropic g and A in their study. Their non-standard (D , E) set was compared with two rhombic standard sets of $Mn(H_2O)_6^{2+}$ (in 10^{-4} cm^{-1}): (231, 60) in $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and (274, 55) in $MgSiF_6 \cdot 6H_2O$ taken from the review by Bowers and Owen [55]. The crystallographic axes were identified by preliminary X-ray analysis. The crystal is monoclinic with $\beta = 91^\circ 55'$ so, in fact, the crystallographic axis system (CAS) (a , b , c) does not form a Cartesian axis system. Importantly, in such cases a suitably modified CAS*, i.e. with one – for monoclinic crystals (or two - for triclinic crystals) selected axis (axes) modified so to obtain a Cartesian axis system, must be used instead of CAS [45, 56]. The modified CAS* may then be adopted as the laboratory axis system (LAS) for EMR measurements. This point has either been overlooked in [54] or in view of small departure of β from 90° the axes (a , b , c) may be considered as approximately forming a Cartesian axis system. The EMR spectra were taken in the ab - and bc -planes. The orientation of the principal axis system (PAS) of the 2nd-rank ZFS ($\mathbf{S.D.S}$) terms (PAS-D), defined with the z -axis as the direction of the maximum spread of the EMR spectrum, was experimentally determined [54] relative to the axes (a , b , c). However, the orientation of the x - and y -axes was not provided for PAS-D.

Although more recent data exist for these ion-host systems, we refrain from full data comparison since the focus is on illustration of the inappropriateness of direct comparisons of standard and non-standard ZFSPs. The

authors [54] note that their values of (D , E) are quite different that the values cited from [55]. It turns out that fitting of the ZFSP sets in question yielded values lying in different areas of the parameters space. Apart from standardization, consideration of low symmetry aspects [56] would be necessary for better understanding of the structural information that could be extracted from EMR spectra.

Mn^{2+} : $NaHSO_4$

Sunandana [57] used only the ZFS parameters D and E , and the isotropic g and A in his study. Some discrepancies in SH parameters in earlier studies [58, 59] were discussed in [57]. EMR measurements were taken rotating crystal about '*the long axis (x) and two other mutually perpendicular axes in the yz plane*', whereas '*the shortest edge in the yz plane*' was also invoked. This suggests that CAS was ascertained from morphology of the single crystal sample. However, since $NaHSO_4$ belongs to the triclinic system and instead of CAS (a , b , c) a suitably modified CAS*, as defined above - with two selected axes modified so to obtain a Cartesian axis system, should have been used to identify experimentally the orientation of PAS-D. It is not clear if the LAS used in [57] was indeed a Cartesian axis system. Note also that no discussion of the symmetry-adapted axis system (SAAS) [45, 56] for the metal site has been provided. Hence, the experimentally determined orientation of the PAS-D (x , y , z) may only be considered as an approximation in view of the low symmetry aspects [45, 56]. The discrepancies in SH parameters [58, 59] discussed in [57] concern, e.g. D and E of [57] that differ significantly from those in Mn-doped alkali-metal sulphates [57], quote: ' *D being smaller in the present case by two-thirds and E being several times larger*'. The claim that '*the large E value indicates that the crystal field is nearly orthorhombic*' is not justified in view of the standardized ZFSP values in Table 2.

Mn^{2+} : $Mg [C_4H_3O_4]_2 \cdot 6H_2O$ (MHMH) & Mn^{2+} : $Ni [C_4H_3O_4]_2 \cdot 6H_2O$ (NHMH)

For the two systems in question Krishna et al. [60] and [61], respectively, used a truncated spin Hamiltonian with D and E , whereas only one 4th-rank cubic ZFS parameter a thus neglecting the two remaining 4th-rank ZFSPs [3, 4]. Both papers contain several misconceptions and possibly wrong relations, which must be clarified. In [60] the small b_{kq} 's were explicitly equated in their Table 1 to D ($=b_2^0$) and E ($=b_2^2$), thus disregarding the usual conventional to b_{kq} 's conversions in Eq. (3), whereas in [61] in their Table 1 no equality sign appears: D (b_2^0) and E (b_2^2) – the representation can be taken for correspondence of the ZFSPs and not the equality, which would be true. In both [60, 61] an incorrect the relation a ($=b_4^0$) appears. Clarification of misinterpretation involving the cubic ZFSP a has recently been dealt with in [62]. Assuming misprints in the relations in [60, 61], for calculations in Table 2 we take the original values as expressed in the conventional notation. Two non-standard ZFSP sets in [60, 61] require the standardization transformations S2/S5.

A note of caution is appropriate concerning the CF=ZFS confusion, which consists in naming the *actual* ZFS related quantities as *supposedly* the 'crystal field' related quantities. This confusion is widely spread in EMR literature as reviewed in [3-5] as well as in magnetism literature as reviewed more recently in [63, 64]. Instances of the CF=ZFS confusion are evident in several phrases in [60], e.g.: ' *E ($=b_2^2$) represents rhombic component of the crystal field*'. Similarly, no such information as: '*strength and nature of the crystalline field*', '*the z -axis of the crystal field*'; pertaining to the CF quantities can be inferred from EMR data – the authors misinterpret the *actual* ZFS quantities for the *supposedly* CF-related ones.

Both systems exhibit monoclinic space group symmetry and thus a suitably modified CAS*, i.e. with one crystallographic axes (usually the c -axis) taken as perpendicular to the remaining two axes, should be adopted

instead of CAS (a, b, c), which does not form a Cartesian axis system [56]. No modified CAS* has been defined in [60, 61]. The procedure to extract SH parameters from EMR spectra used in [60, 61] amounts in fact to an experimental determination of PAS-D (x, y, z) from EMR spectra in two planes. The authors [60, 61] do not mention about carrying out an X-ray orientation of the crystal, so most probably an unoriented single crystal sample was used. The experimentally determined orientation of the PAS-D (x, y, z) and the relative orientation of (a, b, c), or more properly the modified CAS*, and (x, y, z) may only be considered as an approximation in view of low symmetry aspects [45, 56]. The quality of such approximation is hard to judge since additionally only truncated 4th-rank ZFS terms have been included in fittings. Note that the terminology: ‘the z-axis of the crystal field’, called also ‘the principal z-axis of the Mn^{2+} complex’, is inappropriate since this axis has the meaning of the principal z-axis of the **D** tensor only. The PAS of **D** and the PAS of **g** may not coincide each with other and neither PAS-D nor PAS-g need to be directly related to the ligands – metal ion bonds in crystal [65, 66, 67, 68].

It appears that the orthorhombic SH has been used in [60, 61] rather as an *a priori* assumption without proper justification. No consideration of the local site symmetry and the symmetry adopted axis system (SAAS) was provided in [60, 61]. Therefore the resulting ZFSP values are only approximate and may not reflect the actual local site symmetry, which may be lower than orthorhombic. Thus the conclusion that the ZFSPs indicate orthorhombic distortion of the ML_n complex is not convincing, since it is rather a consequence of the assumed orthorhombic SH form. Importantly, the temperature dependence of *D* and *E* observed by EMR was discussed in terms of the structural changes, e.g. ‘the rhombic component of the crystal fields around the manganese ions is quite large’, ‘The higher the values of the ZFS parameters, *D* and *E*, imply greater bonding between the Mn^{2+} metal ion and the water dipoles surrounding it’. [60]. Such structural conclusions must be verified in view of the standardized ZFSP values in Table 2.

Most of the above criticism pertinent for Krishna et al. [60] applies also to [61], except the less evident CF=ZFS confusion. Additionally ‘spin-quenching concept’ is invoked, which should be replaced rather by ‘orbital momentum quenching’, see, e.g. [1, 2]. It is incorrect to ascertain in [60] that for the non-Kramers ions in low symmetry the complete quenching occurs when all the spin degeneracy is removed by the spin-orbit coupling and crystal field. Spin states of the non-Kramers ions, i.e. the Kramers doublets, can be only split by the external magnetic field.

Mn^{2+} : $ZnKPO_4 \cdot 6H_2O$ (ZPPH) & Mn^{2+} : $ZnNH_4PO_4 \cdot 6H_2O$ (ZAPH)

Anandalakshmi et al. used a truncated spin Hamiltonian with the ZFSPs: *D*, *E*, *a*, and *F* in their study of Mn^{2+} in two structurally similar crystals ZPPH [69] and ZAPH [70]. The presentation of SHP values data in table 3 of [69] and [70] is confusing since the components of the SH tensors are mixed with single parameter values. At first glance the ZFSPs [69, 70] appear non-standard, but closer inspection of the data reveal that some of the values listed under the heading *D* do not represent *D* itself. It turns out that the ‘present study’ *D* values were not provided explicitly. Instead, the three unlabelled diagonal components of the **D** tensor (first listed in their Table 2) are repeated in their Table 3 under the heading *D*, whereas the values of the parameter *E* are provided separately.

For ZPPH [69] the ZPSP values given in their table 2 are in [mT], whereas in their table 3 in [10^{-4} cm^{-1}]. It appears that an approximated conversion factor of 10, instead of 9.35 (taking *g* value as 2.0023) [3], was used in [69] to convert the units, while in [70] only the units [mT] were used. In view of this approximation we have used the conversion factor [3] of 9.34 (taking *g* value as 2.0). The principal values of the second-rank tensors in table 2 of [69] and [70] were additionally verified by independent diagonalization using the module 3DD [45] and found to

agree well to within the roundings. Then, adopting various labeling of the components $\{D_i\}$ as $\{D_z, D_y, D_x\}$, the values $\{D_i\}$ were recalculated to (D, E) [3], thus yielding both the standard and non-standard ZFSP sets. The value of E given by the authors [69, 70] corresponds to one specific labeling of $\{D_i\}$ considered by us. Our calculations using the values $\{D_i\}$ (in mT) provided in the abstracts in [69, 70]: $\{D_{xx} = 15.49, D_{yy} = 0.22, D_{zz} = -15.71\}$ in [69] yield $D = -23.565, E = 7.635$ (compares well with $E = 7.64$ in [69]), and $\{D_{xx} = -12.28, D_{yy} = -2.09, D_{zz} = 14.37\}$ in [70] yield $D = 21.555, E = -5.095$; the rounded value $E \sim -5.1$ disagrees with $E = 6.1$ in [70]. Apart from discrepancy in sign, this suggests that the value $E = 6.1$ in [70] might be misprinted. According to the conventions provided in Sec.1, to obtain positive λ the components D_{xx} and D_{yy} in [69, 70] should be swapped. Importantly, it turns out that the sets (D, E) inferred in this way from the data on (D_i, E) listed in [69, 70] are standard.

Checking the cited values of (D, E) for NHMH at 300 K in table 3 of [70] (see our Table 2), it appears that the value $D = 21.60$ (in mT) recalculated from the original (see Table 2) $D = 216$ (in 10^{-4} cm^{-1}) of [61] is correct (using the approximated conversion factor of 10). However, the value $E = 2.89$ (in mT) recalculated from the original $E = 289$ (in 10^{-4} cm^{-1}) of [61] is incorrect; the former value should be $E = 28.9$ (in mT). Similarly, the value $E = 3.47$ (in mT) for MHMH at 300 K in table 3 of [70] recalculated from the original $E = 347$ (in 10^{-4} cm^{-1}) of [60, 61] is incorrect; the former value should be $E = 34.7$ (in mT). Surprisingly, the incorrectly recalculated values of E of [60, 61] match better with the authors' [70] own value $E = 6.1$ (in mT), so misprinted for $E \sim 5.1$ (see above). Concerning the ZFSP set (in mT) for ZAPH of [71] cited in [70]: $\{D_i\} = \{53.52, -35.41, -18.11\}$ and $E = 8.67$, our calculations using labeling $\{D_{zz}, D_{yy}, D_{xx}\}$, respectively, yield $D = 80.28, E = 8.65$ (mT) or $D = 749.6, E = 80.8$ (10^{-4} cm^{-1}). As noted by the authors [70], this standard set [71] highly disagrees with their own results of [70], however, this set [71] compares better with the standardized values in Table 2 for Mn^{2+} ions in other systems.

According to the authors [69, 70] the single crystal rotations along the three orthogonal axes have indicated orthorhombic symmetry and were fitted with orthorhombic spin-Hamiltonian. The low symmetry effects are implicitly evident in the EMR spectra, so have not been explicitly discussed in [69, 70]. Thus the orthorhombic symmetry may be considered only as an approximation. A relatively large E value obtained in [69] supposedly '*indicates deviation from axial symmetry, as also noticed in g and A values.*' We note that in the first place the value of D should be provided for such conclusions. However, since our reanalysis above indicates several discrepancies the ZFSP values: the authors' own ones provided for ZPPH in [69] and ZAPH in [70] as well as the values cited in [69, 70] should be treated with caution.

The 'distortion axis' matched fairly well with one of the Zn-O bond direction in the lattice. The authors [69] stated that the 'distortion axis' for the impurity has been identified along one of the Zn-O bond directions in the crystal. The methodology for determination of the 'distortion axis' seems doubtful (see next subsection). However, the authors [69] are aware that since they have neglected some minor terms in the equation in calculating the angles, these angles give only a rough idea about the direction of the distortion axis and for further correlation. Further confirmation of the 'distortion axis' with the X-ray structure of the host-lattice would be needed.

$\text{Mn}^{2+}:(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$

Kripal et al. [72] used only the ZFSPs D, E , and a . Mn^{2+} was expected to be substituted for NH_4^+ corresponding to an associated pair $\text{Mn}^{2+}\text{-O}^{2-}$, where O^{2-} occupies a nearest neighbor site. The local site symmetry was assumed as orthorhombic. If the upper and lower limits of the estimated errors of the ZFSPs (D, E) are taken into account (see, Table 2) a non-standard set is also obtained: $E/D = (85+2)/(257-2) = 0.3412$. Thus such ZFSP sets constitute near 'border' cases. To illustrate this 'border' aspect two additional sets arising from the upper and lower limits of the

experimental ZFSPs are included in our analysis (see Table 2). Standardization transformation for the non-standard set is S2/S5.

Other comments are pertinent for the study [72] as follows. The origin of the fine structure as resulting “*from the crystal field and the spin–spin interactions*” is not quite correct since as recent microscopic spin Hamiltonian studies [73, 74] reveal the spin-orbit interactions contribute dominantly to ZFS, whereas the contribution from the spin-spin interactions is rather minor. The determination of the direction cosines of the distortion axis using the method of Rao and Subramanian [75] used in [72] appears to be valid only for the cases of axial distortions of six-fold nearly cubic ML_6 complexes. It seems inapplicable to the cases of orthorhombic distortions dealt with in [72]. Detailed considerations of the method [75] and its implications will be dealt with in a separate paper. Consequently, the structural conclusions [72] concerning the distortion axis and its relationship with the direction cosines of some NH_4-O bonds shall be revisited.

Mn^{2+} : $KHSO_4$

Kripal et al. [76] studied this system at 77 K and determined the ZFSPs D , E , and a . In their SH the term $F(a)$ described as “*small correction term due to the cubic portion of the crystalline field*” was used, so in Table 2 the value a (cubic ZFSP) is listed. A distorted octahedral substitutional site was predicted for the Mn^{2+} species. The axis of symmetry is probably slightly tilted from the [001] direction because of a nearby anion vacancy in the [100] or [110] direction. Standardization transformation is S2/S5. The above conclusions on Mn^{2+} : $(NH_4)_2C_2O_4 \cdot H_2O$ study [72] concerning the distortion axis and its relationship with the direction cosines of some bonds apply also to the study of Mn^{2+} : $KHSO_4$ [76] and shall be revisited accordingly.

Mn^{2+} : $ZnMTH$

Raju et al. [77] used a truncated spin Hamiltonian with D and E , whereas only one 4th-rank cubic ZFS parameter a . In their Table 1 two sets of (g ; A ; D , E ; a) for temperature 123 K (non-standard) and 273 K (standard) were presented together with data of others for Mn^{2+} ions in similar systems (all standard). While proper terminology was used for the ‘*zero-field splitting parameters*’ D and E , the parameter a was named confusingly [3, 5, 62] as “*the cubic crystal field parameter ‘a’*.” For the “*biquadratic term*”, i.e. the 4th-rank cubic ZFS term different axes were used “*the four-fold axes for the cubic part of the crystal field*”, whereas the 2nd-rank ZFS terms were expressed in the axes (X , Y , Z). From a systematic study of the angular variation of EPR spectra performed in the three mutually orthogonal planes namely XY , YZ and ZX planes, the principal axes (X , Y , Z) of the complex that Mn^{2+} ions form in the crystal were found by searching the direction of the maximal splitting of the EPR spectra. This procedure means that the axes (X , Y , Z) were not related *a priori* with any SAAS. Since neither the orientation of the sample w.r.t. CAS nor SAAS were discussed, most probably an un-oriented sample was used for EMR study. Thus the ZFSPs [77] may be considered as expressed in an undefined ‘*nominal*’ axis system [39]. The authors presented variation of the ZFSP D as a function of temperature in the range 123 to 413 K for Mn^{2+} : $ZnMTH$. It is observed that D value increases with decreasing temperature. This finding was attributed to the thermal contraction of the lattice, whereas the positive D and a finite E were identified with a compressed octahedron distorted orthorhombically. The corresponding temperature variation of E must be studied in order to fully assess the behavior of the rhombicity ratio with temperature. Then the structural conclusions [77] may need to be revised in view of the standardization.

4. Conclusions

The present study deals with direct standardization of the orthorhombic zero-field splitting (ZFS) parameters available in literature for Mn^{2+} ions in various hosts. The results are systematically tabularized, whereas pertinent comments on implications of standardization are provided in text for each host system. The standardized ZFSP values in Table 2 for Mn^{2+} ions in various systems enables global comparison across data taken from various sources. Careful analysis of the directly comparable ZFSP sets enable identification and clarification of some misinterpretations that yield ambiguous and unreliable results in some papers. Whenever applicable, we have also discussed the intricate low symmetry aspects involved in the EMR studies under review. It has been shown that some approaches used for low symmetry ion-host systems may be considered, at best, as an approximation. Proper methodology for analysis and modeling of EMR data for transition ions at low symmetry sites in crystals is to be discussed in the forthcoming review [78], whereas low symmetry aspects in EMR in [79].

Major conclusion is that direct comparisons of orthorhombic ZFS parameter (ZFSP) sets are only meaningful for sets expressed in a specific *nominal* axis system. Our study reveals that for meaningful comparisons of the ZFSP sets not only the commonly implicitly assumed tenets, i.e. *‘regardless of local site symmetry, ZFSP sets obtained by various authors using different methods should be directly comparable for the same ion-host system as well as for closely related systems provided they are expressed in the same operator notation and units’*, must be satisfied. Moreover, another tenet, arising from peculiar features of orthorhombic ZFS Hamiltonians and embodied in the standardization idea, plays an important role, namely, *‘ZFSP sets are intrinsically comparable only if they belong to the same region of the parameter space, most conveniently if they are expressed in the same nominal axis system within the standard range of the rhombicity ratio’*. The latter tenet has not been fully realized by several researchers, thus leading to meaningless comparisons of the ZFSP sets.

It has been shown that the standardization idea facilitates meaningful comparison of the values of ZFS parameters obtained from different sources and thus helps to avoid confusion. Hence the standard range for the ZFS parameters as well as the crystal field ones is recommended for data presentation arising from EMR spectroscopy studies. The alternative physically equivalent ZFS sets, calculated using the package CST for conversions, standardization, and transformations of ZFS parameters, may serve as input for applications of the multiple correlated fitting technique in follow-up EMR studies. Independent fittings starting from various areas of parameter space, to which each alternative set belongs, may improve reliability of final fitted ZFSPs. Our consideration may help the multiple correlated fitting technique becoming more often used in the EMR and optical spectroscopy area. Importantly, all general conclusions presented above concern also the crystal-field (CF) parameters arising from optical spectroscopy studies.

The methodology presented here and the quantitative results enable more reliable analysis, comparison, and fitting of ZFSP sets from EMR spectra for Mn^{2+} ions in various hosts exhibiting sites of orthorhombic or lower symmetry. In addition to the ten Mn^{2+} doped systems considered here, our literature search indicates about twenty other papers where non-standard ZFS parameters have been reported for Mn^{2+} ions. Many more references reporting non-standard ZFS parameters for other transition-metal and rare-earth ions in crystals may be provided on request from one of us (CZR).

Table 2

Listing of the original ZFSP values and units for Mn^{2+} ions in various hosts. Alternative ZFSPs sets (in the Stevens notation and units of 10^{-4} cm^{-1}) for Mn^{2+} ions in various hosts exhibiting orthorhombic site symmetry obtained using the standardization transformations starting from the non-standard experimental ZFSP sets. Standardized ZFSP sets (in bold) correspond to the values of $|\lambda'|$ below 1.

Ion-host system	Ref	Original		[10 ⁻⁴ cm ⁻¹]		S1 / S3		S2 / S5		S4 / S6		
		D	E	[Units]	D	E	B ₂ ⁰	λ'	B ₂ ⁰	λ'	B ₂ ⁰	λ'
K ₂ SO ₄	[50]	598	-580	[G]	558.4	-541.6	186.1	-/+2.91	177.8	-/+3.09	-363.9	-/+8.4
		660	-559	[G]	616.3	-522.0	205.4	-/+2.54	158.3	-/+3.60	-363.7	-/+0.13
		615	-575	[G]	574.2	-536.9	191.4	-/+2.81	172.8	-/+3.22	-364.2	-/+0.05
Mg(H ₂ O) ₆ H ₂ EDTA	[54]	610	478	[10 ⁻⁴ cm ⁻¹]	610	478	203.3	-/+2.35	-340.7	-/+0.19	137.4	-/+3.96
NaHSO ₄	[57]	309	113	[10 ⁻⁴ cm ⁻¹]	309	113	103.0	-/+1.10	-108.0	-/+0.91	5.0	-/+42.2
MHMH 300 K	[60]	312	347	[10 ⁻⁴ cm ⁻¹]	312	347	104	-/+3.34	-225.5	-/+0.08	121.5	-/+329.5
		414	190	[10 ⁻⁴ cm ⁻¹]	414	190	138	-/+1.38	-164.0	-/+0.68	26.0	-/+302.0
NHMH 300 K	[61]	216	289	[10 ⁻⁴ cm ⁻¹]	216	289	72	-/+4.01	-180.5	-/+0.20	108.5	-/+2.33
77 K		244	390	[10 ⁻⁴ cm ⁻¹]	244	390	81.3	-/+4.80	-235.7	-/+0.31	154.4	-/+2.05
ZPPH	[69]	-23.565 ^{a)}	-7.635 ^{a)}	[mT]	-220.0	-71.3	-73.3	-/+0.97	72.3	-/+1.03	1.0	-/+145.6
ZAPH	[70]	21.555 ^{b)}	5.095 ^{b)}	[mT]	201.3	47.6	67.1	-/+0.70	-57.1	-/+1.35	-10.0	-/+124.2
	[71]	80.28 ^{c)}	8.65 ^{c)}	[mT]	749.6	80.8	249.9	-/+0.32	-165.4	-/+2.02	-84.6	-/+415.3
		257	85	[10 ⁻⁴ cm ⁻¹]	257	85	85.7	-/+0.99	-85.4	-/+1.01	-0.4	-/+171.1
(NH ₄) ₂ C ₂ O ₄ ·H ₂ O	[72]	255 ^{d)}	87 ^{d)}	[10 ⁻⁴ cm ⁻¹]	255	87	85	-/+1.02	-86	-/+0.98	1.0	-/+171
KHSO ₄	[76]	59	32	[10 ⁻⁴ cm ⁻¹]	59	32	19.7	-/+1.62	-25.9	-/+0.53	6.2	-/+45.6
		240	97	[10 ⁻⁴ cm ⁻¹]	240	97	80	-/+1.21	-88.5	-/+0.81	8.5	-/+168.5
ZnMTH 123 K	[77]	225	73	[10 ⁻⁴ cm ⁻¹]	225	73	75	-/+0.97	-74.0	-/+1.03	-1.0	-/+149.00
273 K												

a) Values recalculated by us from $\{D_i\}$; original [69] $E = 7.64$ (see text).

b) Values recalculated by us from $\{D_i\}$; original [70] $E = 6.1$ (see text).

c) Values recalculated by us from values of [71] cited in [70] $\{D_i\}$; cited [70] $E = 8.67$ of [71] (see text).

d) Values arising from taking into account experimental uncertainties (see text).

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