ORTHORHOMBIC STANDARDIZATION OF ZERO-FIELD SPLITTING (ZFS) PARAMETER SETS FOR TRANSITION-METL CENTRES IN VARIOUS HOSTS

S. P. Singh[1*] and Dhananjai Yadav[2]

[1]Department of Physics, Dr B. R. Ambedkar Govt. Degree College, Mainpuri-205001, India
[2]Faculty of Physics in Applied Sciences Department, BBS College of Engineering & Technology, Allahabad, India

*Email: singh525sps@yahoo.com

ABSTRACT

The intrinsic properties of orthorhombic Hamiltonians have enabled derivation of transformation relations for Hamiltonian parametersexpressed in various related axis systems. In this paper the standardization transformations are used to obtain alternative physically equivalent yet numerically distinct parameter sets for transition metal ions (Ni^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}) in various hosts showing orthorhombic or lower site symmetry. Out of six alternative sets one parameter set satisfies the standardization criteria. Importantly, the standardized sets should be used for direct comparisons. Various non-standard ZFS parameter (ZFSP) sets for transition metal ions in crystals are standardized. 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. The calculated alternative sets are presented for seven transition metal ion complexes considered. The results enable more reliable analysis, comparison, and fitting of ZFSP sets from EPR spectra for transition metal ions in various crystals.

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

INTRODUCTION

The standardization idea was originally introduced in EMR for the second-rank conventional ZFS terms on the basis of 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 axes [1-8]. The standard range $0 \leq \lambda \leq 1/3$ corresponds[9] in terms of the diagonal components of the conventional ZFS D tensor (*S.D.S*) [10, 11] to $|D_{XX}| \leq |D_{YY}| \leq |D_{ZZ}|$, whereas $-1/3 \leq \lambda \leq 0$ corresponds[12] 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) [13-16]. The convention $0 \leq \lambda \leq 1/3$ is mostly used in EMR studies of transition-metal ions[17]. The standardization idea has also been introduced in optical spectroscopy and the number of pertinent applications for the orthorhombic CF parameters is growing steadily[18, 19, 20]. The standardization is done using the method discussed in Ref. [21].

*Author for correspondence

The paper is divided into different sections. 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 EPR studies for transition metal ions in various hosts showing orthorhombic site symmetry are considered. Calculations are performed by the package CST for conversions, standardization, and transformations of ZFS (or CF) parameters[22, 23]. Conclusions are provided in Section 4.

Basic Nomenclature and Theoretical Aspects

The extended Stevens (ES) operators, which include both the positive and negative q components, have been defined and their transformation properties determined[24]. 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[25].

For arbitrary low, i.e. triclinic, site symmetry the spin Hamiltonian, including the Zeeman electronic (Ze) terms and ZFS ones in the ES operator notation [3, 24, 25] is defined as [1-5]:

$$H_{spin} = H_{Ze} + H_{ZFS} = \mu_B \boldsymbol{B.g.S} + \sum_{k=2,4,6} \sum_{q=-k}^{k} B_k^q \, O_k^q$$

(S_X, S_Y, S_Z).　　　　　...(1)

Transformations between the g_{ij}–factorsand ZFS parameters expressed in different axis systems (X, Y, Z) are given in Ref. [26]. The "scaled" b_k^q parameters [1-5] are used in literature:

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

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

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

The ligand (crystal) field Hamiltonian H_{CF} can be expressed mathematically in the same form as H_{ZFS} in Eq. (1) upon replacement of the spin operator $\boldsymbol{S}$ by the angular momentum $\boldsymbol{L}$ or $\boldsymbol{J}$ [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 rhombicity ratio $\lambda \equiv E/D$ or alternatively $\lambda' \equiv B_2^2 / B_2^0 \equiv b_2^2 / b_2^0$ plays a crucial role in description of the intrinsic features of ZFS (CF) Hamiltonians for orthorhombic or lower symmetry[27, 28]. There exist three mutually perpendicular and equivalent symmetry axes for orthorhombic symmetry groups $(C_{2v}, D_2,$ and $D_{2h})$[29, 31]. 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)[31] 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 found, 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, similar procedure is adopted as in[21]. Correlation of the axis systems assigned to experimentally determined ZFSP sets may be possible through comparison with model calculations using, e.g. superposition model analysis[32-34], which must be carried out in a well-defined axis system, usually the crystallographic one.

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[35, 36]. 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, 37, 38, 39]) since $[B_2^0] = [B_2^0] = \pm 1/2\{ B_2^2 \}$. 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[40]. The number of applications of the standardization idea [6-10] has been growing since its comprehensive extensions appeared[27, 28]; see the papers[18-20] and references therein.

Applications:

In this section we consider several examples of application of the standardization idea to the orthorhombic 2nd-rank ZFS parameters for transition metal ions (Ni^{2+}, Cr^{3+}, Mn^{2+}) in various hosts with orthorhombic site symmetry. 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 [41, 42].

The alternative sets, calculated using the package CST [22, 23], may serve for application of the multiple correlated fitting technique[28, 31] in future EMR studies. All alternative sets are physically equivalent and give 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 ZFSPs has recently appeared [43].

As a reference notation for the ZFSPs we adopt here B_k^q and units of [10^{-4} cm^{-1}] following the recommendations for unification of notations and guidelines for data presentation in EMR branch[3, 4, 44]. The appropriately converted and then transformed ZFSP sets together with the original ZFSP values and units (for verification) are listed in Table 1. 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 1 (indicated in bold) correspond to the values of $|\lambda'|$ below 1. Hence the standardization transformations (S2/S5 or S4/S6) that give 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.

Ni^{2+}: (NH$_4$)Ni(SeO$_4$)$_2$.6H$_2$O

Grffiths and Owen[45] studied Ni^{2+}: (NH$_4$)Ni(SeO$_4$)$_2$.6H$_2$O attemperatures290 K and90 K. The spectra are adequately explained by crystalline electric field of rhombic symmetry. There are two inequivalent Ni^{2+} ions in unit cell situated at the points (0, 0,0); (1/2, 1/2, 0). As the two ions in unit cell have reflection symmetry in the ac-plane, so that the two sets of rhombic axes are reflection of each other in the ac-plane. It is the two sets of rhombic axes are equally inclined to the susceptibility axes (K$_1$, K$_2$, K$_3$). To determine the axes, therefore, the positions of the absorption lines were found for 5^0 or 10^0 intervals in the direction of H in the planes K$_1$K$_2$, K$_2$K$_3$, K$_3$K$_1$ and the plane containing K$_1$ and the line bisecting K$_2$K$_3$ (hereafter called the 45^0 plane). When cutting the crystal sections the angle between K$_1$ and the c-axis was taken to be as given by Krishnan et. al[46]. The values of this angle found from the positions of the rhombic axes agree with Krishnan's value with in the experimental accuracy.

In the ammonium selenate a small rotation of the two sets of axes in opposite directions about K$_2$ is zero, but there is a rotation of 5^0 about K$_1$, so that x and y lie in the K$_2$K$_3$ plane and K$_2$Oy$_2$=40^0, K$_2$Ox$_1$=40^0. The best fit of these experimental transitions at 290 K and 90 K are obtained by taking D = -1.89 cm^{-1}, -1.73 cm^{-1} and E = -0.79 cm^{-1}, -0.82 cm^{-1}, respectively. These values are non standard the standardization transformation are S2/S5 as given in Table 1.

Mn^{2+}: NaCl

Morigaki et. al.[47]. studiedMn^{2+}: NaCland found the values of ZFSPs. The complexes diffuse through the lattice to form aggregates of Mn^{2+} ions. The symmetry is considered to be rhombic. The zero field splitting parameters of Mn^{2+} ion accompanying a Na$^+$ vacancy at one of its nearest neighbour positions have been obtained as: D = 137.9±1 gauss and E = 51.4±0.4 gauss. These are non-standard parameters the standard values obtained using transformations S2/S5 are given in Table 1.

Cr^{3+}: MgO

Grffiths et. al[48]. studied Cr^{3+}:MgOat X band and 90K.This system is attributed to a Cr^{3+} ion in a rhombic field, there being six ions per unit cell (differing only in orientation of the axes), and fitted by rhombic spin Hamiltonianwith $|D|$= 0.031±0.002 cm^{-1}and $|E|$= 0.22 ±0.01 cm^{-1},a typical set of axes being 'x axis 110, y axis 1$\bar{1}$0 and z axis 001. The spectra for x and y axes are nearly identical. This accounts for the occurrence of pairs of lines along a 110 axis, as each 110 type axis is an x axis for one ion and a y axis for another. It seems reasonable to assume that the observed rhombic field is produced by a lattice defect near the Cr^{3+} ion. The standard sets of ZFSPs and transformation S2/S5 obtained by us is given in Table 1.

Cr^{3+}: AgBr

Cook et. al.[49] also studied Cr^{3+}: AgBrand obtained the ZFSPs.The principal spectrum P* at 95 K was assigned to an orthorhombic centre with axes in <100> directions and accounted for approximately 75% of the resonant intensity. The x axis was taken to correspond to the direction of maximum splitting. The high-field fine-structure lines from centers with B parallel to x or z directions are relatively unaffected by second and higher-order corrections and were used to calculate D and E which were assumed to have opposite signs as in the case of Cr^{3+} : AgCl. The identification of S2* with a centre with a principal axis x in a <110> direction was made on the basis of a line which reached a maximum field of 0.648 T for B parallel to a <110> direction and similar low-intensity line at 0.535 T for B parallel to a <100> direction. At 300 K the D and E parameters of P* had decreased by 15% and 30% respectively. The centre most likely to give the large orthorhombic distortion is that with two vacancies on <100> axes making an angle of 90^0 and the Cr^{3+} ion displaced along the <110> line between

the vacancies. It is probable that for small ions the lattice energy in AgCl and AgBr is lowest for interstitial incorporation. The high preference of Cr^{3+} for octahedral coordination forces it into the substitutional site. The outer fine structure lines of P* and S2* broadened as the temperature was increased. D and E parameters of P*(95 K & 300 K) and S2*(95 K) are 110.8 mT, 66.8 (mT); 91 mT, 61mT and 102 mT, 72 mT respectively which are non standard. The standard values using transformations S2/S5 are given in Table 2.

Cr^{3+}: AgCl

Cook et. al[49]. studied Cr^{3+}: AgCland obtained the ZFSPs. The principal spectrum P consists of a central group of three lines with two outer fine–structure groups of three lines and accounts for about 75% of the total intensity. The angular variation of the low-field lines in P for rotation in a (100) plane is shown figure 3[49] for those angles where the lines did not overlap significantly. P has one axis z in a <100>direction and the remaining two mutually perpendicular axes (x, y) in directions 4^0 away from the cube axes (x', y').

The lines were fitted to the spin Hamiltonian appropriate to the orthorhombic symmetry of the spectrum. The quoted values of the spin Hamiltonian parameters for orthorhombic symmetry are those which give the maximum spread of the spectrum in the xy plane. The displacement of the spectrum axes from the crystal axes in the xy plane indicates that Cr^{3+} centre has monoclinic symmetry. The z lines reach extreme fields in a <100> direction and the y lines at 40^0 away from the cube axis. The term in E appears only in third order for the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions for B parallel to z. D was calculated from the splitting of these lines. E was calculated and checked from the separation of lines which reached extreme fields at B parallel to x and y. The derived parameters of the spin Hamiltonian D and E of P (95 K & 300 K) and S2 (95 K) are 30.5 mT, 14.8 mT; 32mT, 14.7 mT and 33.5 mT, 19.7 mT respectively which are non standard set of parameters and standard set of ZFSPs are given in Table 2 having transformations S2/S5.

Cr^{3+}:BaTiO$_3$

K. A. Muiller and W. Berlinger[50] studied the system Cr^{3+}:BaTiO$_3$ In the orthorhombic Amm2 phase, there are 12 ferroelectric domains with polarization vector along the <110> general cubic directions. The Cr^{3+} EPR spectra have their principal axial vector z'' parallel to the polarization vector, i. e. along a [110] direction for $P\parallel$ [110] plus a smaller

orthorhombic component parallel to [001]. The ZFS parameters at 280 K are obtained as $D_0 = 185.0 \times 10^{-4}$ cm^{-1}, $E_0 = 32.0 \times 10^{-4}$ cm^{-1}. In each ferroelectric phase, there exists an explicit polarization dependence DO^P as well as temperature dependence D_O^T and therefore the temperature variation $D_O(T)$ may be represented as : $D_O(T) = D_O^P + D_O^T$. In orthorhombic phase $D_O^P = 123 \times 10^{-4}$ cm^{-1}, $E_O^P = -101 \times 10^{-4}$ cm^{-1} where as the measured quantity $E_O = +32 \times 10^{-4}$ cm^{-1}. Similar to $D_O(T)$, $E_O(T)$ and E_O^P may be related by $E_O(T) = E_O^P + E_O^T$. Thus, $E_O^T = (32 \times 10^{-4} - E_O^P) \approx 133 \times 10^{-4}$ cm^{-1}. The determined parameters in orthorhombic phase D_O^P and E_O^P are obtained as 123 $\times 10^{-4}$ cm^{-1} and -101×10^{-4} cm^{-1} respectively which are non standard. The standard ZFS parameters obtained with transformation S4 / S6 are given in Table 1.

Fe^{3+}:BiVO$_4$

The non-standard D and E for Fe^{3+} in BiVO$_4$[Table I of51] are standardized (Table 1). Site symmetry is taken approximately to be orthorhombic. The larger value of Fe^{3+} than that of Mn^{2+} [52] indicates that Fe^{3+} substitutes for V^{5+} in BiVO$_4$. The sign of D has changed from positive to negative after the transformation S2.

CONCLUSIONS

The present study provides direct standardization of the orthorhombic zero-field splitting parameters (ZFSPs) available in literature for transition metal ions (Ni^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}) in various host systems. The results are systematically tabulated, whereas necessary comments on implications of standardization are presented in text. The standardized ZFSP values in Table 1 for transition metal ions (Ni^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}) in various host systems enable universal comparison of data taken from different studies. Careful analysis of directly comparable ZFSP sets provides clarification of some misinterpretations that give ambiguous and unreliable results.

It has been shown that the standardization idea helps to avoid confusion and provides meaningful comparison of the values of ZFSPs obtained from different studies. The alternative physically equivalent ZFSP sets may serve as input for applications of the multiple correlated fitting techniques in future EPR and optical studies. The conclusions presented above concern also the crystal-field (CF) parameters arising from optical studies. The quantitative results obtained enable more reliable analysis, comparison, and fitting of ZFSP sets from EPR spectra of transition metal ions (Ni^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}) in various hosts showing orthorhombic site symmetry.

Ion-host system	Ref	Original			[10⁻⁴ cm⁻¹]			S1 / S3			S2 / S5			S4 / S6	
		D	E	[Units]	D	E	B_2^0	B_2^2	λ'	B_2^0	B_2^2	λ'	B_2^0	B_2^2	λ'
Ni²⁺ : (NH₄) Ni(SeO₄)₂.6H₂O 290K	[50]	-1.89	-0.79	[cm⁻¹]	-18900	-7900	-6300	-/+7900	+/-1.25	7100	+/-5500	+/-0.77	-800	+/-13400	-/+16.75
90K		-1.73	-0.82	[cm⁻¹]	-17300	-8200	-5766.7	-/+8200	+/-1.42	6983.3	+/-4550	+/-0.65	-1216.7	+/-12750	-/+10.48
Mn²⁺ : NaCl|	[51]	137.9	51.4	[G]	128.9	47.8	43	+/-47.8	+/-1.11	-45.4	-/+40.6	+/-0.89	2.4	-/+88.4	-/+36.83
Cr³⁺ : MgO	[52]	310	2200	[10⁻⁴ cm⁻¹]	310	2200	103.3	+/-2200	+/-21.29	-1151.7	+/-945.1	-/+0.82	1048.4	-/+1254.9	-/+1.20
Cr³⁺ : AgBr	[53]	110.8a)	66.8	[mT]	1035.3	624.2	345.1	+/-624.2	+/-1.81	-484.7	-/+205.6	+/-0.42	139.6	-/+829.8	-/+5.95
		91b)	61	[mT]	850.3	569.9	283.4	+/-569.9	+/-2.01	-426.7	-/+140.2	+/-0.33	143.3	-/+710.2	-/+4.96
		102c)	72	[mT]	953.1	456.8	317.7	+/-456.8	+/-1.44	-387.2	-/+248.2	+/-0.64	69.5	-/+704.9	-/+10.14
Cr³⁺ : AgCl 95K	[53]	30.5d)	14.8	[mT]	285	138.3	95	+/-138.3	+/-1.46	-116.6	+/-73.4	+/-0.63	21.7	-/+211.7	-/+9.78
300K		32e)	14.7	[mT]	299	137.4	99.7	+/-135.4	+/-1.38	-118.5	-/+80.8	+/-0.68	18.9	-/+218.2	-/+11.58
		33.5f)	19.7	[mT]	313	184.1	104.3	+/-184.1	+/-1.76	-144.2	-/+64.5	+/-0.45	39.9	-/+284.6	-/+6.23
Cr³⁺ : BaTiO₃	[54]	123	-101	[10⁻⁴ cm⁻¹]	123	-101	41	-/+101	-/+2.46	30	-/+112	-/+3.73	**-71**	-/+11	+/-0.15
Fe³⁺ : BiVO₄	[55]	1401.9	2339	[10⁻⁴ cm⁻¹]	1401.9	2339	467.3	+/-2339	+/-5.01	**-1403.2**	**+/-468.6**	-/+0.33	935.9	-/+1870.5	-/+1.99

Table 1: Listing of the original ZFSP values and units for transition metal ions in various host systems. Alternative ZFSPs sets (in the Stevens notation and units of 10^{-4} cm⁻¹) for transition metal 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 $|\lambda'|$

-a) represents spectrum P* at 95K
b) represents spectrum P* at 300K
c) represents spectrum S2*
d) represents spectrum P at 95K
e) represents spectrum P at 300K
f) represents spectrum S2

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