Supplemental Material for: Importance of the fourth-rank zero field splitting parameters for Fe^{2+} (S = 2) adatoms on CuN/Cu(100) surface evidenced by their determination based on the DFT and experimental data

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Derivation of formulas

Here the derivation from[1] is briefly summarized. For S=2 orthorhombic sites, solving $\widehat{H}_{ZFS}$ gives five energy levels λ_i expressed as:

$$\begin{aligned} \lambda_a &= 2D \\ \lambda_b &= -D-3E \\ \lambda_c &= -D+3E \\ \lambda_d &= 2\sqrt{D^2+3E^2} \\ \lambda_e &= -2\sqrt{D^2+3E^2} \end{aligned}\quad , \tag{S1}$$

if $\widehat{H}_{ZFS}$ is expressed in conventional form and:

$$\begin{aligned} \lambda_a &= 6B_2^0+12B_4^0-12B_4^4 \\ \lambda_b &= -3B_2^0-3B_2^2-48B_4^0+12B_4^2 \\ \lambda_c &= -3B_2^0+3B_2^2-48B_4^0-12B_4^2 \\ \lambda_d &= 42B_4^0+6B_4^4+2\sqrt{9(B_2^0-5B_4^0+B_4^4)^2+3(B_2^2+3B_4^2)^2} \\ \lambda_e &= 42B_4^0+6B_4^4-2\sqrt{9(B_2^0-5B_4^0+B_4^4)^2+3(B_2^2+3B_4^2)^2} \end{aligned} \tag{S2}$$

if $\widehat{H}_{ZFS}$ is expressed in the form of Stevens' operators. The obtained wavefunctions are linear combinations of functions $|S, M_S\rangle$, therefore M_S cannot always be treated as good quantum number. Hence the formulas for λ_i in Eq. (S1) can be assigned unequivocally to the energy levels only if standardization convention $|D| > 3|E|$ is obeyed and the signs of ZFSPs D and E are assumed. When the eigenvalues in Eq. (S1) and eigenfunctions are analyzed with the assumption $|D| > 3|E|$, changing the sign of ZFSP D, causes substantial changes in the general look of energy level diagram, while changing the sign of parameter E merely makes levels λ_b and λ_c "swap places".

For $S = 2$, irrespective of the sign of D, the following relations can be deduced from the standardization convention $|D| > 3|E|$: $\lambda_e < -2|D| \leq \lambda_a$ and $\lambda_a \leq 2|D| < \lambda_d$. Consequently, the inequality: $\lambda_e < \lambda_a < \lambda_d$ holds true. Also, , if $E > 0$, then $\lambda_b < \lambda_c$. Then, we consider different signs of D to deduce additional relations:

1. if $|D| > 3E$ and $D > 0$, then $-2D < \lambda_b < \lambda_c < 2D = \lambda_a$
2. if $|D| > 3E$ and $D < 0$, then $\lambda_a = 2D < \lambda_b < \lambda_c < -2D$

This indicates that eigenstates can be ordered with increasing energy values, in two ways: for $D > 0$: $\lambda_e < \lambda_b < \lambda_c < \lambda_a < \lambda_d$ and for $D < 0$: $\lambda_e < \lambda_a < \lambda_b < \lambda_c < \lambda_d$, with the ground state's energy always being described by formula λ_e, although the quantum number M_S assigned to it is different for opposite signs of D. When D is positive the ground state should be treated as having $M_S = 0$, but when D is negative the ground it is best described as one of the energy levels forming a Kramer's doublet $M_S = \pm 2$.

If we want to order λ_is from Eq. (S2) in a similar way, apart from adopting the standardization rules, we also have to assume that the magnitudes of the 2nd-rank ZFSPs are significantly larger than those of the 4th-rank ZFSPs: $|B_2^q| \gg |B_4^q|$. Then all the reasoning done for $S = 2$ systems described by conventional parameters presented above can be repeated. This is possible, because for $|B_2^q| \gg |B_4^q|$ the values of λ_i from Eq. (S2) approach that of λ_i described by conventional parameters – Eq. (S1). Therefore, it can be stated that λ_e is always the energy of the ground state and two λ_i schemes are possible. For $B_2^0 > 0$ (tantamount to $D > 0$) and $B_2^2 > 0$ (tantamount to $E > 0$) we obtain the sequence: $\lambda_e < \lambda_b < \lambda_c < \lambda_a < \lambda_d$ and for $B_2^0 < 0$ (tantamount to $D < 0$) and $B_2^2 > 0$ the eigenvalues are ordered: $\lambda_e < \lambda_a < \lambda_b < \lambda_c < \lambda_d$.

Next the ground state has to be set to 0 with all the other energy levels adjusted accordingly, by defining the spin excitation energy of spin state i as:

$$E_i = \lambda_i - \lambda_e, \tag{S3}$$

where $i = a, b, c, d, e$ signifies any one of the eigenstates. Thus for $\widehat{H}_{ZFS}$ expressed in Stevens' operators we obtain the relations $E_i\ (= \lambda_i - \lambda_e) \propto B_k^q$ as:

$$\begin{cases} E_a = 6B_2^0 - 30B_4^0 - 18B_4^4 + 2\sqrt{9(B_2^0 - 5B_4^0 + B_4^4)^2 + 3(B_2^2 + 3B_4^2)^2} \\ E_b = -3B_2^0 - 3B_2^2 - 90B_4^0 + 12B_4^2 - 6B_4^4 + 2\sqrt{9(B_2^0 - 5B_4^0 + B_4^4)^2 + 3(B_2^2 + 3B_4^2)^2} \\ E_c = -3B_2^0 + 3B_2^2 - 90B_4^0 - 12B_4^2 - 6B_4^4 + 2\sqrt{9(B_2^0 - 5B_4^0 + B_4^4)^2 + 3(B_2^2 + 3B_4^2)^2}. \\ E_d = 4\sqrt{9(B_2^0 - 5B_4^0 + B_4^4)^2 + 3(B_2^2 + 3B_4^2)^2} \\ E_e = 0. \end{cases} \tag{S4}$$

In this system of equations $E_i, i = a - d$ represent the energy levels of excited spin states of S=2 spin system at zero field (the energy of the ground state is set to zero). If values of the spin excitation energies ($E_i, i = a - d$), are known from the experiment or theoretical modeling, we obtain a system of equations containing four equations and five variables – ZFSP (B_k^q). Such system is underdetermined and to make it solvable we applied two approaches. The first one was to reduce the number of variables, by assuming that one of the 4th-rank ZFSPs is equal to zero: $B_4^0 = 0$, $B_4^2 = 0$ and $B_4^4 = 0$. The second one was to add new non-redundant relations to the system, namely to fix the ratio between parameters B_2^2 and B_4^2, by adding equations: $200B_4^2 = B_2^2$, $20B_4^2 = B_2^2$ and $2B_4^2 = B_2^2$ to the system. The so-modified six systems were solved, yielding sets of inverse equations, i.e. B_k^q as functions of energy levels at zero field, which were published in Table A3 of[1]. Here we only recall one of those sets – obtained for the $b_4^4 = 0$ option – Eq. (S5). (In light of our calculations presented in[1] neglecting the ZFSP b_4^4 seems to be the best option).

$$\begin{cases} B_2^0 = -\frac{E_b}{42} - \frac{E_c}{42} + \frac{E_a}{7} - \frac{E_d}{21} \\ B_2^2 = -\frac{E_b}{14} + \frac{E_c}{14} \pm \frac{2\sqrt{3}\sqrt{\pm E_a(\mp E_a \pm E_d)}}{21} \\ B_4^0 = -\frac{E_b}{210} - \frac{E_c}{210} - \frac{E_a}{210} + \frac{E_d}{140} \\ B_4^2 = \frac{E_b}{42} - \frac{E_c}{42} \pm \frac{\sqrt{3}\sqrt{\pm E_a(\mp E_a \pm E_d)}}{42} \\ B_4^4 = 0 \end{cases} \tag{S5}$$

Three general observations can be made when analyzing Eq. (S5): firstly, the presence of ± signs signals that more than one set of solutions is possible, secondly, the presence of square roots implies that, theoretically, for some input values of E_i it might be possible that B_k^q come out complex, lastly the fact that some formulas are linear functions of E_is and some are power functions suggests that some parameters might be more sensitive to the input values than the others. These observations refer not only to Eq. (S5) above, but to all the others presented in Table A3 of[1].

Application of formulas

For completeness we provide here all tables, including those presented in main text.

TABLE S1. The values of the spin excitation energies reported in Table III of[2] recalculated from [meV] to [cm^{-1}].

DFT approach	E_a	E_b	E_c	E_d
LSDA+SOC	0.807	9.28	15.57	17.10
LSDA+DMFTSOC (HIA)	0.242	97.43	98.64	110.98
Experiment	1.45	31.46	46.46	52.91

TABLE S2. The ZFSPs b_k^q for Fe^{2+} adatoms on CuN/Cu(100) surface extracted according to method presented in[1] using theoretical data[2]-and experimental ones[3].

Constraint	parameter	Set of energies used LSDA+SOC		LDA+DMFT+SOC (HIA)		Experiment	
$b_4^0 = 0$	b_2^0	-3.87	3.87 (-3.87)	no real solutions		-12.50	-12.50 (-12.50)
	b_2^2	-0.446	3.14 (-3.14)			-1.06	7.49 (-7.49)
	b_4^0	0	0 (0)			0	0 (0)
	b_4^2	-17.96	$-1.77\bullet10^{-2}$ ($1.77\bullet10^{-2}$)			-42.82	$-4.46\bullet10^{-2}$ ($4.46\bullet10^{-2}$)
	b_4^4	$-4.00\bullet10^{-9}$	$-4.00\bullet10^{-9}$ ($-4.00\bullet10^{-9}$)			$1.80\bullet10^{-8}$	$1.80\bullet10^{-8}$ ($1.80\bullet10^{-8}$)
$b_4^2 = 0$	b_2^0	-3.87 (-3.87)	0.552 (-1.85)	-29.82 (-29.82)	1.88	-0.348 (11.43)	2.49 (-12.50)
	b_2^2	3.15 (-3.15)	3.15 (-0.745)	0.605 (-0.605)	0.605	-22.50 (10.73)	-22.50 (-7.51)
	b_4^0	$-1.20\bullet10^{-3}$ ($-1.20\bullet10^{-3}$)	-5.53 (2.77)	-8.44 (-8.44)	-48.08	3.56 (-1.78)	$1.12\bullet10^{-2}$ ($-5.59\bullet10^{-3}$)
	b_4^2	0 (0)	0 (33.18)	0 (0)	0	0 (-21.36)	0 ($-6.71\bullet10^{-2}$)
	b_4^4	$8.40\bullet10^{-3}$ ($8.40\bullet10^{-3}$)	38.71 (-19.35)	-0.594 (-0.594)	276.84	-24.93 (12.46)	$-7.83\bullet10^{-2}$ ($3.91\bullet10^{-2}$)
$b_4^4 = 0$	b_2^0	-3.87	-3.87 (-3.87)	-29.76	-29.76 (-29.76)	-12.50	-12.50 (-12.50)
	b_2^2	-0.45	3.14 (-3.14)	-2.30	2.82 (-2.82)	-1.06	7.49 (-7.49)
	b_4^0	$-5.71\bullet10^{-10}$	$-5.71\bullet10^{-10}$ ($-5.71\bullet10^{-10}$)	-8.53	-8.53 (-8.53)	$2.57\bullet10^{-9}$	$2.57\bullet10^{-9}$ ($2.57\bullet10^{-9}$)
	b_4^2	-17.96	$-1.77\bullet10^{-2}$ ($1.77\bullet10^{-2}$)	-14.54	11.08 (-11.08)	-42.82	$-4.46\bullet10^{-2}$ ($4.46\bullet10^{-2}$)
	b_4^4	0	0 (0)	0	0 (0)	0	0 (0)
$10b_4^2 = b_2^2$	b_2^0	-3.85 (-3.85)	0.534 (-1.87)	-29.82 (-29.82)	1.88	-12.47 (-12.47)	1.75 (-4.70)
	b_2^2	3.21 (-3.21)	3.21 (-0.803)	0.617 (-0.617)	0.617	7.65 (-7.65)	7.65 (-1.20)
	b_4^0	$-2.34\bullet10^{-2}$ ($-2.34\bullet10^{-2}$)	-5.51 (2.79)	-8.44 (-8.44)	-48.08	$-4.13\bullet10^{-2}$ ($-4.13\bullet10^{-2}$)	-17.82 (9.01)
	b_4^2	0.321 (-0.321)	0.321 (32.88)	$6.17\bullet10^{-2}$ ($-6.17\bullet10^{-2}$)	$6.17\bullet10^{-2}$	0.765 (-0.765)	0.765 (106.52)
	b_4^4	0.164 (0.164)	38.55 (-19.56)	-0.593 (-0.593)	276.84	0.289 (0.289)	124.73 (-63.04)
$b_4^2 = b_2^2$	b_2^0	-3.59 (3.76)	0.275 (-2.10)	-29.82 (-29.82)	1.88	-12.03 (-12.03)	1.31 (-5.34)
	b_2^2	3.93 (3.42)	3.93 (-1.55)	0.756 (-0.756)	0.76	9.38 (-9.38)	9.38 (-2.72)
	b_4^0	-0.347 (-0.318)	-5.18 (3.08)	-8.44 (-8.44)	-48.07	-0.593 (-0.593)	-17.27 (9.81)
	b_4^2	3.93 (-4.05)	3.93 (29.13)	0.756 (-0.756)	0.756	9.38 (-9.38)	9.38 (98.91)
	b_4^4	2.43 (2.22)	36.28 (-21.58)	-0.582 (-0.582)	276.83	4.15 (4.15)	120.86 (-68.63)
$b_4^2 = 10b_2^2$	b_2^0	no real solutions		-29.82	1.88 (1.88)	-9.70	-1.02 (4.26)
	b_2^2			-0.605	-0.605 (0.605)	-7.50	-7.50 (2.23)
	b_4^0			-8.45	-48.07 (-48.07)	-3.50	-14.36 (-2.20)
	b_4^2			-6.05	-6.05 (6.05)	-75.01	-75.01 (123.65)
	b_4^4			-0.536	276.78 (276.78)	24.51	100.50 (15.38)

TABLE S3. Values of the ZFSPs B_k^q for Fe^{2+} adatoms on CuN/Cu(100) surface reported in[4] in meV and μeV and converted by us to notation b_k^q and cm^{-1}.

data set	b_2^0 (cm^{-1})	b_2^2 (cm^{-1})	b_4^0 (cm^{-1})	b_4^2 (cm^{-1})	b_4^4 (cm^{-1})
Figure 2a	-12.82	7.74	1.02	4.07	0.871
Figure 2b	-13.07	7.74	0.726	2.66	0.484
Figure 2c	-12.82	7.99	0.581	-0.726	-0.919

Estimating the importance of 4th-rank ZFSPs

TABLE S4. The 2nd-rank ZFSPs from[2] converted to cm^{-1}.

	LSDA+SO (Ref.[2])	LSDA+SOC (Ref.[2])	LSDA+U+SOC (Ref.[2])	Exp. (Ref.[2,3])
b_2^0	-2.90	-3.87	-5.40	-12.50
b_2^2	2.42	3.15	5.32	7.50

TABLE S5. Energy levels (in cm^{-1}) recalculated only from the 2nd-rank ZFSPs obtained in this work and experimental (EXP) ones after standardization (ST)[5].

Constraint		LSDA+SOC ST		LSDA+DMFT+SOC (HIA) ST	EXP ST	
$b_4^0 = 0$	E_4	17.10		No real solutions	52.92	
	E_3	15.56			46.45	
	E_2	9.28			31.47	
	E_1	0.808			1.45	
$b_4^2 = 0$	E_4	17.10	7.59	119.30	51.99	52.92
	E_3	15.57	6.39	90.08	48.84	46.47
	E_2	9.28	4.90	88.87	25.30	31.44
	E_1	0.810	0.0987	0.00409	3.84	1.46
$b_4^4 = 0$	E_4	17.10		119.20	52.92	
	E_3	15.56		92.18	46.45	
	E_2	9.28		86.54	31.47	
	E_1	0.808		0.0891	1.45	
$10b_4^2 = b_2^2$	E_4	17.10	7.72	119.30	52.91	19.02
	E_3	15.61	6.53	90.09	46.58	15.41
	E_2	9.19	4.93	88.86	31.27	13.01
	E_1	0.845	0.113	0.00426	1.52	0.101
$b_4^2 = b_2^2$	E_4	17.00	9.15	119.30	52.76	22.28
	E_3	16.03	8.23	90.23	47.78	19.21
	E_2	8.16	5.12	88.72	29.03	13.76
	E_1	1.31	0.366	0.00639	2.32	0.452
$b_4^2 = 10b_2^2$	E_4	No real solutions		7.63	17.79	
	E_3			7.57	17.41	
	E_2			2.55	6.87	
	E_1			1.34	2.41	

TABLE S6. The differences between energy levels (in cm^{-1}) recalculated from the 2nd-rank ZFSPs obtained in this work and the ones reported in[2].

		LSDA+SOC ST		LSDA+DMFT+SOC (HIA) ST	EXP ST	
$b_4^0 = 0$	E_4	0.00261		No real solutions	0.00506	
	E_3	-0.00225			-0.00640	
	E_2	0.00485			0.0115	
	E_1	0.00130			0.00253	
$b_4^2 = 0$	E_4	0.00261	-9.51	8.32	-0.923	0.00505
	E_3	0.000344	-9.18	-8.56	2.39	0.0115
	E_2	0.000344	-4.38	-8.56	-6.16	-0.0154
	E_1	0.00323	-0.708	-0.238	2.39	0.0115
$b_4^4 = 0$	E_4	0.00261		8.22	0.00506	
	E_3	-0.00225		-6.46	-0.00640	
	E_2	0.00485		-10.90	0.0115	
	E_1	0.00130		-0.153	0.00253	
$10b_4^2 = b_2^2$	E_4	0.00200	-9.38	8.32	0.00405	-33.89
	E_3	0.0465	-9.03	-8.55	0.122	-31.05
	E_2	-0.0819	-4.35	-8.57	-0.184	-18.44
	E_1	0.0385	-0.693	-0.238	0.0681	-1.35
$b_4^2 = b_2^2$	E_4	-0.0971	-7.95	8.32	-0.154	-30.63
	E_3	0.460	-7.34	-8.41	1.32	-27.25
	E_2	-1.11	-4.15	-8.71	-2.43	-17.69
	E_1	0.507	-0.440	-0.236	0.872	-0.999
$b_4^2 = 10b_2^2$	E_4	No real solutions		-103.35	-35.12	
	E_3			-91.07	-29.05	
	E_2			-94.89	-24.59	
	E_1			1.09	0.959	

TABLE S7. The percentage differences between energy levels recalculated by us from the 2nd-rank ZFSPs obtained in this work and the calculated ones[2] and experimental (EXP) ones[3].

		LSDA+SOC		LSDA+DMFT+SOC (HIA)	EXP	
$b_4^2 = 0$	E_4	0.02%		No real solutions	0.01%	
	E_3	-0.01%			-0.01%	
	E_2	0.05%			0.04%	
	E_1	0.16%			0.17%	
$b_4^2 = 0$	E_4	0.02%	-55.60%	7.50%	-1.74%	0.01%
	E_3	0.00%	-58.95%	-8.68%	5.14%	0.02%
	E_2	0.00%	-47.17%	-8.79%	-19.58%	-0.05%
	E_1	0.40%	-87.77%	-98.31%	164.44%	0.79%
$b_4^4 = 0$	E_4	0.02%		7.41%	0.01%	
	E_3	-0.01%		-6.55%	-0.01%	
	E_2	0.05%		-11.18%	0.04%	
	E_1	0.16%		-63.19%	0.17%	
$10b_4^2 = b_2^2$	E_4	0.01%	-54.88%	7.50%	0.01%	-64.06%
	E_3	0.30%	-58.03%	-8.67%	0.26%	-66.83%
	E_2	-0.88%	-46.89%	-8.80%	-0.59%	-58.63%
	E_1	4.77%	-85.96%	-98.24%	4.69%	-93.04%
$b_4^2 = b_2^2$	E_4	-0.57%	-46.51%	7.50%	-0.29%	-57.89%
	E_3	2.95%	-47.13%	-8.53%	2.85%	-58.66%
	E_2	-12.00%	-44.76%	-8.94%	-7.71%	-56.25%
	E_1	62.92%	-54.57%	-97.36%	60.10%	-68.84%

$b_4^2 = 10b_2^2$	E_4	No real solutions	-93.12%	-66.37%
	E_3		-92.33%	-62.52%
	E_2		-97.39%	-78.17%
	E_1		451.51%	66.06%

TABLE S8. The variants considered for assessing significance of the 4th-rank ZFSPs b_4^q.

Variant:	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
b_4^q included:	b_4^0, b_4^2, b_4^4;	b_4^2, b_4^4;	b_4^0, b_4^4;	b_4^0, b_4^2;	b_4^0;	b_4^2;	b_4^4;	none

TABLE S9. The values of ZFSPs (in cm^{-1}) used to assessing the influence of different 4th-rank ZFSPs on energy levels. The ZFSPs b_k^q were taken from[6] for Fe^{2+} ions at Cu$_2$N/Cu(100) and used for test calculations.

b_2^0	b_2^2	b_4^0	b_4^2	b_4^4
-12.51	7.51	0.46	-1.69	2.56

TABLE S10. The spin excitation energy levels (in cm^{-1}) calculated using the ZFSPs listed in Table S9 for variants defined in Table S8.

Variant	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
E_d	52.72	52.29	52.91	53.21	53.40	52.77	52.48	52.96
E_c	45.77	46.25	45.53	46.27	46.03	46.74	46.00	46.50
E_b	30.08	30.55	30.51	30.58	31.01	31.05	30.98	31.48
E_a	0.343	0.355	0.438	1.35	1.45	1.37	0.450	1.46

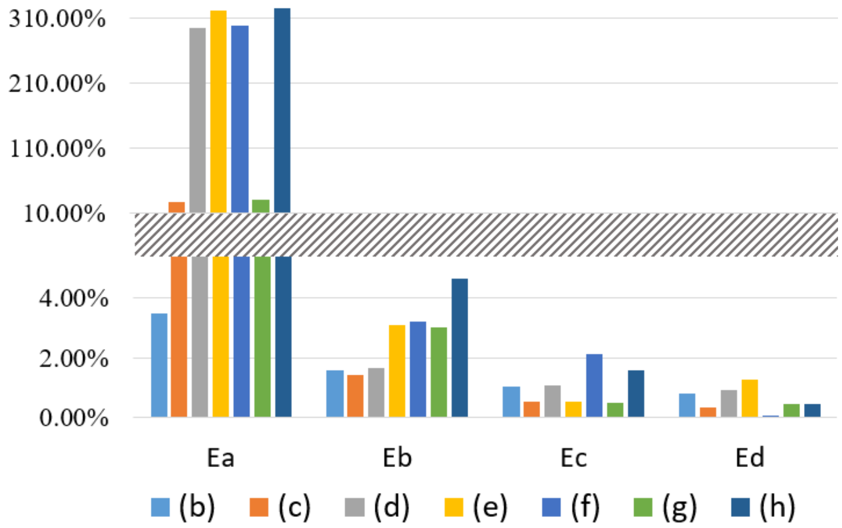

FIG. 1. Diagram showing the absolute differences (in percents) between the respective $\tilde{S} = 2$ spin excitation energies E_i, $i = a$-d, calculated using variant (a) and variants (b) to (h). Note the distinct scale applies to the lower and upper parts as indicated by the shaded box.

Discussion of the terminological confusion

It is important to make readers aware of the terminological confusion, which have crept into the adatoms literature. To facilitate recognition and classification of a particular type of confusion, a generic definition of confusion between two distinct notions: A and B (each being well-defined and predominantly established in a specific area), has been adopted[7–10]. The confusion of the type denoted A=B is defined as the cases of incorrect referral to the quantities associated with one notion B (e.g., ZFS) by the name associated with another notion A (e.g. CF or MA - defined below). In general, the quantities may mean, e.g., effects, Hamiltonians, eigenfunctions, energy, parameters, or energy level splitting. Several important points should be kept in mind.

The major type of confusion is the CF=ZFS confusion, which pertains to the cases of labeling the true ZFS quantities[11–18] as purportedly the crystal field (CF) [or equivalently ligand field (LF)] quantities[19–25].

Due to its long history[26,27], it has been well entrenched in EPR literature as reviewed in[7–9]. The inverse ZFS=CF confusion, which pertains to the cases of labeling the true CF (LF) quantities as purportedly the ZFS quantities, has emerged only recently as discussed in[10]. Important point is that the ZFS Hamiltonian, $\tilde{H}_{ZFS}$, by definition describes, in an *effective* way, the splitting of the spin levels within the ground orbital singlet due to the action of the *physical* Hamiltonian that includes the free-ion, CF/LF, and spin−orbit coupling (SOC) terms[7–18]. The *effective* SH and thus the single-ion $\tilde{H}_{ZFS}$ Hamiltonians act within their own subspace of states of the *effective* spin operator $\tilde{S}$ [7–18]. The description of magnetic properties of the TM- or RE-based systems involves also the notion of magnetic anisotropy (MA) originally defined for bulk magnetic systems[28–30]

The MA phenomenon is quantifiable in terms of the macroscopic quantity called the magnetic anisotropy energy (MAE), which is expressed in terms of the magnetic anisotropy constants K_i[31–36]. Major sources of MAE are due to either single-ion anisotropy (SIA), i.e. equivalently magnetocrystalline anisotropy (MCA), or the anisotropy of exchange interactions. Regardless of the MA origin, MAE is defined as the part of the free energy F_E of the magnetic system that depends on the direction of the magnetization $\boldsymbol{M}$ in crystal. For the $3d^N$ ions with an orbital singlet ground state in crystals, as well as $4f^7$ S-state ions[8], relations can be derived for the MA constants (K_1, K_2) representing them as functions of the respective ZFSPs, see, e.g.[28–36]. Hence, the ZFS parameters associated with the single-ion *effective* spin $\tilde{S}$, $\tilde{H}_{ZFS} \propto (\tilde{S})$ should not be referred to as the MA parameters or constants. The same applies to the ZFS associated with the *effective* total spin $\boldsymbol{S_T}$ of ECS (SMM), $\tilde{H}^T_{ZFS} \propto (\boldsymbol{S_T})$, so the reasoning is more involved[8]. Keeping in mind the above clarifications, the true ZFS parameters may be validly used to characterize the '*magnetic anisotropy*' but shall not be identified with the true MA parameters or constants.

The current situation in magnetism and EMR literature is that a given crucial notion is often referred to by one of three names that are not synonymous: CF (LF), SH (ZFS), or MA. It is evident that in such cases two of three names must be incorrectly used. Such cases constitute confusion of the type: CF=ZFS, ZFS=CF, or MA=ZFS as well as in some cases a compounded confusion: MA=CF/LF=ZFS. Such confusions are unacceptable since each notion has a well-defined meaning in one of the major areas, i.e. optical spectroscopy, EMR, and magnetism, respectively. Regrettably, the ZFS parameters (D, E), which are most widely used in adatoms and magnetism studies, or the equivalent ones in the Stevens notation (B_2^q or b_2^q, q = 0, 2), are often referred to as '*anisotropy parameters'* or '*anisotropy constants'*. Such terminology constitutes the MA=ZFS confusion since the former parameters represent in fact the true orthorhombic ZFSPs[7–18]. Unfortunately, this confusing terminology is prevalent in the adatoms literature discussed herein. Pertinent examples of the MA=ZFS confusion may be found, e.g. in[2–4,37–52]. Recently, the interrelationships between the true ZFSPs (D, E) and MA constants (K_1, K_2) have been clarified in[53], whereas implications of the MA=ZFS confusion have been considered in[54].

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