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Conversions of the Second-Rank Zero Field Splitting Parameters Measured Assuming the Fictitious Spin $S' = 1$ to those for the Effective Spin $\tilde{S} = 2$

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We investigate feasibility of comparison between the zero field splitting parameters obtained experimentally based on the spin Hamiltonian with the fictitious spin $S' = 1$ and those with the effective spin $\tilde{S} = 2$. The former zero field splitting parameters have recently been measured for Fe^{2+} ions in forsterite Mg_2SiO_4, whereas the latter zero field splitting parameters are available in literature, e.g. for Fe^{2+} and Cr^{2+} ($\tilde{S} = 2$) ions. It turns out that no unique direct comparison is feasible and hence appropriate conversion relations need to be derived. Methodology for such conversions is outlined. Various combinations of the possible energy level schemes for the spin $\tilde{S} = 2$ and $S' = 1$ are briefly described. Illustrative preliminary results concerning appropriate conversions of the second-rank zero field splitting parameters measured by high-frequency EMR for Fe^{2+} in natural and synthetic forsterite are presented. Detailed results and full analysis will be given elsewhere.

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1. Introduction

Electron magnetic resonance (EMR) [1, 2] determination of the spin Hamiltonian (SH) parameters for Fe^{2+} ions in natural and synthetic forsterite (Mg_2SiO_4) by Shakurov et al. [3] has been hindered by several factors. The wide-band EMR spectrometer covered a limited frequency region of $\nu = 65$ to 850 GHz, hence only three transitions were detected in the temperature range of 4.2–15 K in the magnetic field up to 9.5 kG. Importantly, these three transitions have been described supposing that, quote [3]: "the system of energy levels has an effective spin $S' = 1$" instead of the effective spin $\tilde{S} = 2$ [4–6] most likely expected for Fe^{2+} ions in low symmetry sites, see, e.g. [7, 8].

Our analysis [9] of the high-frequency EMR (HF-EMR) data [3] reveals that the "spin" value $S' = 1$ has been assigned for Fe^{2+} ions in Mg_2SiO_4 only due to experimental limitations, whereas the approach [3] represents, in fact (see Sect. 2), the *fictitious* spin $S' = 1$ arising from the *effective* spin $\tilde{S} = 2$ states [4–6]. The second-rank zero field splitting (ZFS) parameters [4–6] were obtained by fitting the experimental HF-EMR data using SH with the spin $S' = 1$ [3]. So-obtained axial (D') and rhombic (E') ZFS parameters [3] cannot be directly compared with D and E available in literature for Fe^{2+} ions, which generally exhibit the effective spin $\tilde{S} = 2$ [7, 8]. To enable direct comparison of (D', E') [3] and (D, E) [7, 8], appropriate conversion relations need to be derived for various combinations of the possible energy level schemes for the two spin cases: $\tilde{S} = 2$ and $S' = 1$. Methodology for such derivations is outlined. Various combinations of the possible energy level schemes for the spin $\tilde{S} = 2$ and $S' = 1$ are briefly described.

Illustrative preliminary results of appropriate conversions of the second-rank ZFS parameters measured by HF-EMR for Fe^{2+} in natural and synthetic forsterite [3] will be presented. Since the Fe^{2+} ions in Mg_2SiO_4 exhibit large ZFS, this system may be potentially suitable for application as high-pressure probes [10, 11] for high-magnetic field and high-frequency EMR (HMF-EMR) studies, see, e.g. [12, 13]. These aspects, detailed results and full analysis will be discussed in [9]. Investigation of the role of the fourth-rank ZFS terms, which must be taken into account for spin $\tilde{S} = 2$ [4–6], is now in progress. The results of the extended calculations will be given elsewhere.

2. Theoretical background

2.1. *Effective spin* $\tilde{S} = 2$ *Hamiltonian versus the fictitious "spin"* $S' = 1$ *Hamiltonian*

The distinction between the effective SH approach and that of the fictitious SH approach has been clarified in the reviews [4–6]. Basic definitions of (i) effective spin and effective SH, and (ii) fictitious spin, are also recapped in [9]. For the sake of clarity, distinction between effective spin $\tilde{S}$ and fictitious spin S' is illustrated in Fig. 1. In general, for any specific subset of the ground effective spin states $(2\tilde{S}+1)$ of a paramagnetic ion, a *fictitious "spin"* S' may be ascribed *artificially* to describe this particular subset of distinct N $(N < N_t)$ lowest-lying energy levels out

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*corresponding author; e-mail: michal.kozanecki@amu.edu.pl of the total manifold of N_t energy levels. The *fictitious "spin"* S' is ascribed so that the multiplicity $(2S'+1)$ equals the number N of the selected energy levels, thus $S' = (N-1)/2$.

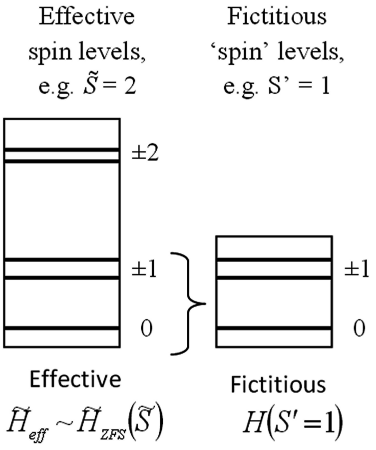

Fig. 1. Visualization of distinction between the effective and fictitious spin levels (adapted from [6]).

For Fe^{2+} ions at octahedral and lower symmetry sites, depending on the crystal-field (CF) strength [14–16], three routes exists, which yield the possible energy level schemes with the ground state corresponding to nominal "spin" $S' = 1$ systems [9]. Note that properly ligand field (LF) is not an alternative name of crystal field (CF), since the latter is a purely ionic account, whereas in the former case covalency effects are included. However, as evidenced in the review [6], the names CF and LF are very often used synonymously in literature.

Transitions between the "spin" $S' = 1$ state may be observed by EMR and related techniques. Our analysis [9] of the HF-EMR data for Fe^{2+} in Mg_2SiO_4 [3] convincingly shows that the "spin" value $S' = 1$ has been assigned only due to experimental limitations. In fact, the approach [3] represents the *fictitious* spin $S' = 1$ arising from the *effective* spin $\tilde{S} = 2$ states [4–6]. In both spin cases for orthorhombic and lower symmetry, the SH expressed in the conventional notation, besides the Zeeman terms, includes the axial (D) and rhombic (E) ZFS terms [4–6]:

$$H_{ZFS} = D[S_z^2 - S(S+1)/3] + E\left(S_x^2 - S_y^2\right). \qquad (1)$$

The implicit adoption of the fictitious spin $S' = 1$ [4–6], which for Fe^{2+} in Mg_2SiO_4 [3] arises from the effective spin $\tilde{S} = 2$ [9], necessitates consideration of several feasible matches of the spin levels as well as the associated wave functions for the two spin cases: $\tilde{S} = 2$ and $S' = 1$.

2.2. Energy levels and wave functions for the spin $\tilde{S} = 2$ and $S' = 1$

Survey of the matrix elements for the $S' = 1$ (spin triplet) and $\tilde{S} = 2$ (spin quintet) systems with either axial (D) or rhombic (D, E) symmetry available in literature, which uncovered some misprints in the earlier sources, has been carried out in [9]. The second-rank ZFS Hamiltonian matrices for $S' = 1$ and $\tilde{S} = 2$ at zero magnetic field were diagonalized by us yielding the energy levels, expressed as functions of the ZFS parameters D and E, and the corresponding wave functions. The possible energy levels schemes were identified [9] assuming the convention $|D| > 3E$ [4–6]. For illustration two selected energy levels for positive ZFS parameter D are presented in Fig. 2. These energies and the selection rules for the allowed transitions between the respective spin states were utilized for derivation of the conversion relations between the ZFS parameter sets for the effective $\tilde{S} = 2$ and the fictitious $S' = 1$. Since the assignments of the measured field-frequency dependences of the resonance transitions to the actual energy levels of the spin $S' = 1$ were not explicitly provided in [3], we utilize the fitted values of the $S' = 1$ ZFS parameters, denoted below as $D_{S=1}$ and $E_{S=1}$, to infer indirectly the feasible assignments. To correlate the assignments for $S' = 1$ with those for $\tilde{S} = 2$ (described by the ZFS parameters $D_{S=2}$ and $E_{S=2}$) several combinations of the $S' = 1$ and $\tilde{S} = 2$ energy levels must be considered. We must also ensure that no other combinations energy levels combinations, which would lead to another possible conversion relations, are feasible. A dilemma arises since the HF-EMR data [3] indicate three transitions but only two transitions may be considered for the $S' = 1$ case. It appears that within the three observed transitions [3] only two are independent. These aspects will be discussed in [9].

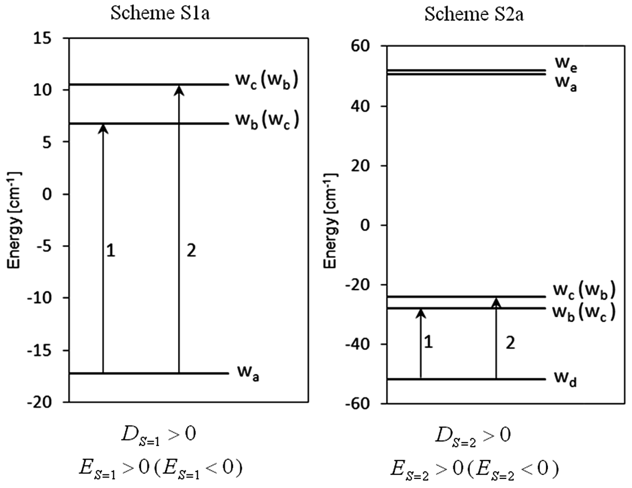

Fig. 2. Selected energy level schemes for the spin $S' = 1$ (left) and $\tilde{S} = 2$ (right) corresponding to the cases $D > 0$.

2.3. Conversion relations

Relations between the ZFS parameter sets for the effective $\tilde{S} = 2$ and the fictitious $S' = 1$ were derived for each combinations of the possible energy level schemes by matching the respective $S' = 1$ and $\tilde{S} = 2$ transitions. The conversion relations for the case where $D_{S=1}$, $E_{S=1}$,

$D_{S=2}$, and $E_{S=2} > 0$ are obtained as

$$D_{S=2} = \frac{1}{3}\left(D_{S=1} + 2\sqrt{D^2_{S=1} - E^2_{S=1}}\right),$$
$$E_{S=2} = \frac{1}{3}E_{S=1}. \qquad (2)$$

The alternative conversion relations have also been obtained [9]. Importantly, the other solution yields the $E_{S=2}$ value differing significantly from $E_{S=1}$, while $D_{S=2}$ approaches $D_{S=1}$ for small values of $E_{S=1}$. Similar findings applicable for the cases with $D_{S=2} < 0$ will be discussed in [9]. In short, the ZFS parameters obtained assuming the fictitious $S' = 1$ are not directly comparable with those determined based on the effective $\tilde{S} = 2$ approach.

3. Results

Application of the conversion relations for reinterpretation of the ZFS parameters ($S' = 1$: D', E') determined for Fe^{2+} in natural and synthetic forsterite [3] in terms of the ZFS parameters ($\tilde{S} = 2$: D, E) has been carried out assuming different ordering of the energy levels. Both Fe^{2+} metal sites ($M1$ (inversion symmetry) and $M2$ (mirror plane symmetry)) [3] have been considered yielding different results for specific combinations of the $S' = 1$ and $\tilde{S} = 2$ energy levels. The selected original and converted ZFS parameters for Fe^{2+} ions at $M1$ sites in Mg_2SiO_4 are presented in Table I. This conversion assumes correspondence of the lowest two transitions for the respective schemes in Fig. 2. Deeper analysis [9] of the EMR data [3] reveals that another assumption may also be valid, i.e. the lowest two transitions for $S' = 1$ matched with the upper two transitions for $\tilde{S} = 2$.

TABLE I

The ZFS parameters for Fe^{2+} ions located at the $M1$ sites in Mg_2SiO_4: original ($D_{S=1}$, $E_{S=1}$) in GHz and converted into cm^{-1} together with the recalculated ($D_{S=2}$, $E_{S=2}$) cm^{-1} for the selected combination of the $S' = 1$ and $\tilde{S} = 2$ energy levels (see text).

ZFS	Original	Converted	ZFS	$D_{S=2}, E_{S=2} > 0$	$D_{S=2}, E_{S=2} < 0$
$D_{S=1}$	–627.39	–20.9275	$D_{S=2}$	20.8864	–6.9347
$E_{S=1}$	48.14	1.6058	$E_{S=2}$	0.5353	–0.5353

4. Discussion and conclusions

To ensure reliability of the ZFS parameters obtained by us for Fe^{2+} ions in Mg_2SiO_4, it is worth to compare them with the experimental or theoretical ZFS parameters available in literature for Fe^{2+} ($\tilde{S} = 2$) ions in several orthorhombic systems. This comparison indicates [9] that, depending on the case $D_{S=2} > 0$ or $D_{S=2} < 0$, the ranges of the ZFS parameters D and E are in good mutual agreement either with the ZFS parameters obtained, e.g. for $(NH_4)_2[Fe(H_2O)_6](SO_4)_2$ or $FeCl_2{\cdot}4H_2O$ and $FeF_2{\cdot}4H_2O$ [8], respectively.

Analysis of the ZFS parameter data available for, e.g. $(NH_4)_2[Fe(H_2O)_6](SO_4)_2$ [17, 18] indicates that the fourth-rank ZFS parameters for Fe^{2+} ions are of significant magnitude. Hence, omission of these parameters in fitting experimental data may substantially change the values of the fitted second-rank ZFS parameters. For this reason, as an extension of the present calculations we shall investigate the role of the fourth-rank ZFS terms, which must be taken into account for the $\tilde{S} = 2$ ions [4–6]. It would be worthwhile to study also the mineral fayalite, i.e. Fe_2SiO_4, which exhibits magnetic properties. The present results shall enable consideration of suitability of the Fe^{2+}:Mg_2SiO_4 and related systems for application as high-pressure probes [10] for HMF-EMR studies [12, 13].

In conclusion, the methodology for derivation of appropriate conversion relations between the axial D' and rhombic E' ZFS parameters obtained based on the fictitious spin $S' = 1$ approach [3] has enabled direct comparison with the ZFS parameters D and E available in literature for Fe^{2+} ions, which are generally described within effective spin $\tilde{S} = 2$ approach.

Acknowledgments

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References

[1] F.E. Mabbs, D. Collison, *Electron Paramagnetic Resonance of d Transition-Metal Compounds*, Elsevier, Amsterdam 1992.

[2] *Multifrequency Electron Paramagnetic Resonance*, Ed. S.K. Misra, Wiley-VCH, Weinheim 2011.

[3] G.S. Shakurov, T.A. Shcherbakova, V.A. Shustov, *Appl. Magn. Reson.* **40**, 135 (2011).

[4] C. Rudowicz, *Magn. Reson. Rev.* **13**, 1 (1987); Erratum: *ibid.* **13**, 335 (1988).

[5] C. Rudowicz, S.K. Misra, *Appl. Spectrosc. Rev.* **36**, 11 (2001).

[6] C. Rudowicz, M. Karbowiak, *Coord. Chem. Rev.* **287**, 28 (2015).

[7] C. Rudowicz, H.W.F. Sung, *J. Phys. Soc. Jpn.* **72**, Supplement B 61 (2003).

[8] M. Zając, I.E. Lipiński, C. Rudowicz, *J. Magn. Magn. Mater.* **401**, 1068 (2016).

[9] M. Kozanecki, C. Rudowicz, *J. Magn. Reson.*, to be published.

[10] P. Gnutek, C. Rudowicz, H. Ohta, T. Sakurai, *Polyhedron* **102**, 261 (2015).

[11] T. Sakurai, K. Fujimoto, R. Matsui, K. Kawasaki, S. Okubo, H. Ohta, K. Matsubayashi, Y. Uwatoko, H. Tanaka, *J. Magn. Reson.* **259**, 108 (2015).

[12] J. Telser, J. Krzystek, A. Ozarowski, *J. Biol. Inorg. Chem.* **19**, 297 (2014).

[13] T. Sakurai, K. Fujimoto, R. Goto, S. Okubo, H. Ohta, Y. Uwatoko, *J. Magn. Reson.* **223**, 41 (2012).

[14] C.A. Morrison, *Crystal Fields for Transition-Metal Ions in Laser Host Materials*, Springer, Berlin 1992.

[15] B.N. Figgis, M.A. Hitchman, *Ligand Field Theory and Its Applications*, Wiley-VCH, New York 2000.

[16] M. Wildner, M. Andrut, C. Rudowicz, in: *Spectroscopic Methods in Mineralogy — EMU Notes Mineralogy*, Vol. 6, Eds. A. Beran, E. Libowitzky, Eötvös University Press, Budapest 2004, Ch. 3, p. 93.

[17] J.C. Gill, P.A. Ivey, *J. Phys. C Solid State Phys.* **7**, 1536 (1974).

[18] M. Zając, C. Rudowicz, *Acta Phys. Pol. A* **132**, 19 (2017).