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Electron magnetic resonance studies of Fe^{3+} ions in BaTiO_3: Implications of the misinterpretation of zero-field splitting terms and comparative data analysis

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The recent electron magnetic resonance studies (EMR) studies [Decker *et al.*, Phys. Rev. B **66**, 174103 (2002)] of Fe^{3+} ions in BaTiO_3 indicate a pronounced discrepancy concerning the values of the fourth-rank zero-field splitting (ZFS) parameters from various authors. Our reanalysis of the ZFS terms for the pertinent symmetry cases reveals a misinterpretation of the ZFS parameters by Decker *et al.* This leads to different ZFS parameter relationships than those originally assumed. Reinterpretation of their EMR results, using the proper conversions relations to the prevailing conventional ZFS notation derived by us, removes the discrepancy in question. This exemplifies the pitfalls arising from such misinterpretation. The ZFS parameters for $\mathrm{Fe}^{3+}:\mathrm{BaTiO}_3$ in various phases are reanalyzed, reconverted as appropriate, and presented in a unified way together with the g-factors. Comparative analysis of the available EMR data for $\mathrm{Fe}^{3+}:\mathrm{BaTiO}_3$ reveals also other inconsistencies in the ZFS notations occurring in the literature, implications of which for data interpretation are discussed.

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I. INTRODUCTION

Barium titanate (BaTiO_3) exhibits three successive phase transitions with decreasing temperature from paraelectric cubic phase to ferroelectric tetragonal phase, then to orthorhombic phase, and to rhombohedral phase at low temperature.[1–3] Pure and doped BaTiO_3 have been extensively studied due to technological applications.[4–6] Recently created unique nanostructure materials based on BaTiO_3 exhibit simultaneously both magnetic and electric ordering, thus offering new promising applications.[7] Electron magnetic resonance (EMR) techniques[8–10] and optical absorption spectroscopy ones[11–13] play an important role in understanding and characterization of the properties of BaTiO_3 doped with various transition metal and rare-earth ions. EMR studies of BaTiO_3 pre-1990 were reviewed by Müller and Fayet,[1] whereas those of $\mathrm{Fe}^{3+}:\mathrm{BaTiO}_3$ based on the spin Hamiltonian (SH) analysis[1,8–11] are comparatively reviewed here. EMR measurements, even without full SH analysis of spectra, provide important information on, e.g., photoconductivity, origin of EMR signals, charge transfer processes, and positive temperature coefficient of resistivity effect.[14–17] Complementary to EMR studies, the crystal-field (CF) and optical spectroscopy studies of BaTiO_3 are also of importance.[2,18,19] The CF energy levels and absorption spectra for Fe^{3+}, Fe^{4+}, and Fe^{2+} ions in the cubic, tetragonal, and orthorhombic phases in BaTiO_3 were studied using the superposition model.[2] The LDA calculations of the CF parameters and the zero-field splitting parameters (ZFSPs) were carried out[20] for Fe^{3+} ions at various sites in BaTiO_3. The studies[2,20] enable correlation of the optical spectroscopy and EMR data.

Recently, Decker *et al.*[21] reported EMR studies of $\mathrm{Fe}^{3+}:\mathrm{BaTiO}_3$ in the ferroelectric phase over a range of pressures and temperatures near the paraelectric-ferroelectric phase transition line. The main objective of their work, i.e., to identify temperature and pressure of the tricritical point of BaTiO_3 using EMR, has been achieved essentially with a higher accuracy than previously. However, the study[21] indicates a pronounced discrepancy concerning the values of the fourth-rank cubic ZFSP for Fe^{3+} ions in BaTiO_3 as compared with other results. The authors[21] could not offer any explanation for this discrepancy. A science citation index search has revealed no citations of the paper[21] as of April 2006. In this paper to solve this discrepancy we carry out a comprehensive comparative analysis of EMR data available for Fe^{3+} ions in the normal form of BaTiO_3 in various phases. The low symmetry aspects involved in EMR studies[22,23] of Fe^{3+} ions in the hexagonal form of BaTiO_3 will be dealt with elsewhere. Since in their SH the authors[21] omitted some operator terms,[24] in Sec. II we reanalyze the SH forms and parameter notations for the symmetry cases pertinent for EMR studies of $\mathrm{Fe}^{3+}:\mathrm{BaTiO}_3$. Conversion relations between the ZFSPs used by Decker *et al.*[21] and the standard conventional ZFSPs[8–10,21] are derived. Our relations differ from the improper ones assumed by the authors. Our literature survey reveals other inconsistencies in the SH notations as summarized in Sec. II. In Sec. III the ZFSP values for Fe^{3+} ions in various phases of BaTiO_3 are reanalyzed, reconverted as appropriate, and presented in a systematic and unified way. The corresponding values of the g factors are also tabularized. Reinterpretation of EMR results[21] using the proper conversions removes the discrepancy[21] in question. Our comparative analysis of EMR data for $\mathrm{Fe}^{3+}:\mathrm{BaTiO}_3$ available in the literature exemplifies the pitfalls arising from misinterpretation of SH forms.

II. SPIN HAMILTONIAN FORMS AND PARAMETER NOTATIONS

Decker *et al.*[21] used a SH including the electronic Zeeman terms and the supposedly tetragonal ZFS terms

$$H = \beta B \cdot \overleftrightarrow{g} \cdot S + DS_z^2 + aS_z^4 + b(S_x^4 + S_y^4), \tag{1a}$$

$$H=\mu_B B\cdot\vec{g}\cdot S+D'S_z^2+a'S_z^4+b'(S_x^4+S_y^4). \tag{1b}$$

In order to distinguish the ZFSPs[21] in Eq. (1a) from the standard conventional ZFSPs,[8–10,24] we add a prime in Eq. (1b), whereas the Bohr magneton β in Eq. (1a) is replaced by the IUPAC recommended[25] symbol μ_B. Note that the parameters D, a, and b (alias D', a', and b') in Eq. (1) were named inappropriately as "crystal field" parameters.[21] As reviewed[10,24,26] such terminology confuses two distinct physical quantities: (i) the *actual* crystal-field Hamiltonian[11–13] and (ii) the *effective* fine structure (or ZFS) Hamiltonian[8–10] as well as the respective Hamiltonian parameters. Unfortunately, this confusion is widely spread in the literature; see the reviews.[24,26] The standard cubic ZFS term for spin $S=2$ or $5/2$ is[8–10,24]

$$H_{cub}=\frac{a}{6}\left(S_\xi^4+S_\eta^4+S_\zeta^4-\frac{1}{5}S(S+1)(3S^2+3S-1)\right), \tag{2}$$

where the constant terms in Eq. (2) are sometimes omitted. For tetragonal symmetry we have

$$H_{tetr}=D\left[S_z^2-\frac{1}{3}S(S+1)\right]+H_{cub}+\frac{F}{180}\{35S_z^4-[30S(S+1)-25]S_z^2-6S(S+1)+3S^2(S+1)^2\}. \tag{3}$$

The last term in Eq. (3) represents the fourth-rank axial ZFS term. In general, the z axis in the axial second- and fourth-rank ZFS term may not coincide[24] with any of the cubic axis (ξ,η,ζ) in Eq. (2).

Equivalent form of the SH (3) in terms of the extended Stevens (ES) operators[24,27] $O_k^q(S_x,S_y,S_z)$, which are nowadays most widely used in EMR studies,[8–10,24,26–28] is

$$H_{tetr}=B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4. \tag{4}$$

In EMR literature the ZFS parameters b_k^q defined with the uniform scaling factors f_k as[24,27]

$$\tilde{H}_{ZFS}=\sum_{kq}f_kb_k^qO_k^q,\quad B_2^q=\frac{1}{3}b_2^q,\ \text{and}\ B_4^q=\frac{1}{60}b_4^q \tag{5}$$

are often alternatively used. SH in Eq. (4) can also be represented with the fourth-rank cubic and axial terms separated[24] as in Eq. (3)

$$H'_{tetr}=B_2^0O_2^0+\tilde{B}_4(O_4^0+5O_4^4)+\tilde{B}_4^0O_4^0, \tag{6}$$

with the new parameters defined[24] as

$$\tilde{B}_4^0=B_4^0-\frac{1}{5}B_4^4,\quad \tilde{B}_4=\frac{1}{5}B_4^4. \tag{7}$$

When the cubic axes (ξ,η,ζ) in Eqs. (2) and (3) coincide with the tetragonal axes (x,y,z) in Eqs. (4) and (6) the following relations arise:[24]

$$B_2^0=\frac{1}{3}D,\quad B_4^0=\frac{a}{120}+\frac{F}{180},\quad B_4^4=\frac{a}{24}; \tag{8a}$$

$$b_2^0=D,\quad b_4^0=\frac{a}{12}+\frac{F}{3},\quad b_4^4=\frac{5}{2}a. \tag{8b}$$

Various other conventional SH forms appearing in the literature have been reviewed,[24] whereas incorrect relations between the conventional second-rank ZFSPs and the tensor operator ones were discussed.[28] Klein and Schwartz[29] used a SH similar to that in Eq. (6) but omitted the symbol "$\sim$" over their axial parameter B_4^0. This creates a potential confusion, since the actual $B_4^0\neq\tilde{B}_4^0$ [see Eq. (7)]. Note that the operator terminology in the review[21] is confusing since the existing well-established definitions of the tensor operators[24,26] are disregarded.

Decker *et al.*[21] oversimplify comparison of the ZFS terms and conclude that the parameter a of Müller and Berlinger,[30] who use Eq. (2), is six times larger than that defined by them in Eq. (1a), i.e., supposedly the following relation holds:[21]

$$a[\text{Eq. (2)}]=6a'[\text{Eq. (1b)}]. \tag{9}$$

Comparing the temperature and pressure dependence of the average value of $\langle a'\rangle=(a'+2b')/3$ the authors[21] discuss a disagreement with the results of Müller and Berlinger,[30] quote: "*in order to compare with the values given in that paper* (Ref. 30 here) *we must recognize that the term which they label a is six times larger than the parameter which we labeled a* [i.e., a' in Eq. (1b)]. *However, even after dividing their values by 6 to compare with our results, their results are still a factor of 2–3 times larger than ours*." They admit later "…*we do not know why their results differ* (Ref. 30 here) *so much from ours*." Below we provide a solution of this discrepancy.

A survey of pertinent literature reveals that Decker *et al.*[21] used SH (1a) originally proposed by Hornig *et al.*[31] in 1959, who have chosen this notation for simplicity; quote: "*There appears to be no standard notation for the tetragonal field case. For the cubic field case a=b corresponds to a/6 in Refs. 4 and 5*." Note that Bleaney and Stevens[32] (their[21] Ref. 5) used Eq. (2). It seems that the usage by Decker *et al.*[21] of the early nonstandard SH, Eq. (1a), was unnecessary in view of the existing complete SH forms for tetragonal symmetry. Conventional SH notations for various symmetry cases, e.g., Eqs. (2) and (3), as well as various tensor operator notations, e.g., the ES operators[24,27] in Eqs. (4) and (6), have been reviewed.[10,24,26–28] The nonstandard definition[31] of a must have been recognized by Sakudo,[33] who correctly recalculated, using implicitly Eq. (2), the value[31] of a but provided no explanation. Our analysis (see Sec. III) reveals that the Sakudo's[33] value of a is in good agreement with the experimental data of others. Note that the SH form used by Sakudo[33,34] corresponds to Eq. (2), but the last "-1" is most probably misprinted as "+1." To obtain the SH eigenenergies the authors[21] used the Jacobi method and then a second-order perturbation. It may be useful to reanalyze the raw spectral data[21] using one of the EMR-related computer programs available in the public domain.[35]

It turns out that the relation in Eq. (9) is based on an incorrect equivalence of the third term in Eq. (1) and the whole cubic SH in Eq. (2). From Eqs. (1)–(3) it follows that only for cubic symmetry the last two terms in Eq. (1a) (with $D'=0$ and up to the constant term) yield equivalently $a'=b'=\frac{a}{6}$ of Eq. (2). However, for tetragonal symmetry the a $[a']$ term in Eq. (1a) and (1b) does not represent the "cubic" part, as assumed[21] deriving Eq. (9). This term corresponds to the fourth-rank axial F term in Eq. (3). This is the b $[b']$ term, which corresponds to the cubic term in Eq. (2). Decker *et al.*[21] also claim that "*in the cubic phase the crystal field parameters* $a=b$ (actually the ZFS ones[24,26]), *but they separate discontinuously or with an initial infinite slope upon entering the tetragonal phase, depending on the order of the transition*." The first part of this statement is true, since the equality $a=b$ holds in the cubic phase. However, the second part would need a reinterpretation in the case when the F-term in Eq. (3) would be properly included in the SH in Eq. (1a) for the tetragonal phase. Then one should also take $a=b$ due to the explicit separation of the cubic and axial terms.

The consequences of the non-standard SH (Ref. 21) in Eq. (1) become clear when one rewrites the fourth-rank ZFS terms in Eq. (1b) in the form

$$H^{IV}=(a'-b')S_z^4+b'(S_z^4+S_x^4+S_y^4). \qquad (10)$$

Omitting the constant terms that do not affect the energy levels Eqs. (10) and (3) yield the relations

$$D'=D-\frac{F}{180}[30S(S+1)-25], \qquad (11)$$

$$a'=\frac{a}{6}+\frac{35}{180}F, \qquad (12)$$

$$b'=\frac{a}{6}. \qquad (13)$$

The inverse conversion relations, which are needed for analysis of the ZFSPs for $Fe^{3+}:BaTiO_3$ in Sec. III are

$$D=D'+\frac{1}{35}(a'-b')[30S(S+1)-25], \qquad (14)$$

$$a=6b', \qquad (15)$$

$$F=\frac{36}{7}(a'-b'). \qquad (16)$$

Several important points arise. The SH (1a) used in Ref. 21 represents an implicit omission in the axial fourth-rank F term in Eq. (3) of the S_z^2 part and constants. Such omission induces a fourth-rank correction to the second-rank ZFSP D' accounted for by the second term in Eq. (11). Equation (9) is invalid and should be replaced by Eq. (15) [or Eq. (13)], whereas a more involved relation, Eq. (12), applies for the parameter a'. Hence, the statement:[21] "*The assumption of* $b-a$ $[b'-a']$ *being proportional to* D $[D']$ *seems reasonable*" turns out to be incorrect, since $[b'-a']$ depends on F not D.

Below we provide also the rhombic ZFS terms, since they have been employed for Fe^{3+} ions in the normal[33] and hexagonal[22,23] form of $BaTiO_3$. Orthorhombic SH in the ES operator notation[27] is[8–10,24,26]

$$H_{\mathrm{orth}}=B_2^0O_2^0+B_2^2O_2^2+B_4^0O_4^0+B_4^2O_4^2+B_4^4O_4^4. \qquad (17)$$

In the conventional notation[24] the second-rank axial and rhombic terms in Eq. (17) are

$$H_{\mathrm{orth}}=D\left[S_z-\frac{1}{3}S(S+1)\right]+E(S_x^2-S_y^2). \qquad (18)$$

For $Fe^{3+}:BaTiO_3$ in the cubic and tetragonal phase E vanishes, whereas is measurable in the orthorhombic phase.[33] Instead of a unique conventional notation equivalent to the rhombic fourth-rank ZFSP B_4^2, a variety of symbols exists:[24] $B_4^2=4C$ (Ref. 36), K (Ref. 37), $K/36$ (Ref. 38), $4b_2$ (while $B_4^0=b_0$ $B_4^4=2b_4$) (Ref. 39), $H/3$ (Ref. 40), $T/3$ (Ref. 41), and $4C_{42}=4C$ (Ref. 42).

Our literature survey reveals also an unusual cubic SH[43]

$$H_{cub}=a^s\left(S_x^4+S_y^4+S_z^4-\frac{1}{5}S(S+1)(3S^2+3S-1)\right). \qquad (19)$$

The superscript "s" is added to the original[43] parameter a (a^s) in Eq. (19) to distinguish it from (i) the usual a in Eq. (2) and (ii) the nonstandard[21] a' in Eq. (1b). The form (19) implies: $a^s=\frac{a}{6}$; thus it adds up to the confusion concerning the cubic ZFS parameter discussed above. Since the earlier papers by Sastry[44,45] contain the correct SH form, Eq. (2), most probably a in Ref. 43 is a misprint for $\frac{a}{6}$. The values[44,45,33] of a for $Fe^{3+}:BaTiO_3$ (tetragonal phase) and a^s in Ref. 43 turn out to be compatible with each other.

Finally, we discuss the tensor operator notation used by Rimai and deMars[46] (R/M) for the tetragonal SH

$$H=b_{2,0}Y_{2,0}+b_{4,0}Y_{4,0}+b_{4,4}(Y_{4,4}+Y_{4,-4})+b_{6,0}Y_{6,0}+b_{6,4}(Y_{6,4}+Y_{6,-4}). \qquad (20)$$

Comparison[24] of the definitions[46] of $Y_{l,m}=Y_{l,m}(S)$ with the ES operators[27] yields $b_{l,m}(\mathrm{R/M})=b_k^q(\mathrm{ES})$; $l=k$, $m=q$.

III. ANALYSIS AND REINTERPRETATION OF EXPERIMENTAL EMR DATA

Any meaningful data comparison requires consideration of various factors that bear on their interpretation and comparability. Three groups of such factors can be identified for the experimental SH parameters: (1) *sample-related factors:* sample preparation method, domain structure, space group symmetry, existence of impurities and/or defects, and the nature of the observed paramagnetic centers; (2) *external factors:* magnetic field, pressure, and temperature; (3) *factors inherent in EMR measurements:* SH form used (operator and parameter notations), axis system adopted, and numerical methods of analysis and resolution of EMR spectra. To ensure the SH parameter comparability, we attempted to extract all pertinent factors and provided them either in tables or in text below. However, often the authors do not provide all pertinent factors.

First we discuss the general and more extensive aspects not suitable for presentation in tables. Concerning the local positions of Fe^{3+} ions in $BaTiO_3$ and their site symmetry, in most cases Fe^{3+} ions replace Ti^{4+} ions, although different Fe^{3+}-V_0 (vacancy) centers were also dealt with both theoretically and experimentally.[20] Following the recommendations[47,48] based on the reviews,[10,24,26,49] we have chosen the parameters b_k^q in Eqs. (5) and (8b) as the reference notation and the units of $[10^{-4}\ \mathrm{cm}^{-1}]$ for comparative data presentation. After proper conversions and/or recalculations, the reported ZFSPs (Refs. 20, 21, 29, 31, 33, 34, 43, 45, 46, and 50) are listed chronologically in Table I together with the g factors. Similarly, in Table II we present the theoretical ZFSPs from the LDA calculations.[20]

Horning *et al.*[31] used SH in Eq. (1a), however, to avoid misinterpretation of the ZFSP symbols below we use D', a', and b' of Eq. (1b). The authors[31] observed several EMR resonance transitions at frequencies 9.5 GHz and 16.3 GHz (originally: kmc/s=GHz). For direct comparison the ZFSP values[21,31] are given both in units of $[\mathrm{cm}^{-1}]$ and [GHz]. Using the approximated relation[31] and keeping only the terms linear in a''' and b', they could resolve the quantities (at room temperature): $|\Delta| \equiv |2D' + 17a' + 11b'| = 0.195 \pm 0.004\ \mathrm{cm}^{-1}$ (5.85 GHz) and $12a + 9b = 0.032 \pm 0.007\ \mathrm{cm}^{-1}$ (0.96 GHz). The values obtained at each frequency agree to within the experimental accuracy. Temperature dependence of $|\Delta|$ in Fig. 7 of Ref. 31 shows a steady decrease from the room-temperature $T = 26\ ^\circ\mathrm{C}$ value to about $|\Delta| = 0.092\ \mathrm{cm}^{-1}$ (2.7 GHz) at $T = 120\ ^\circ\mathrm{C}$, whereas in the cubic phase ($T = 120-170\ ^\circ\mathrm{C}$) $|\Delta|$ is constant: $|\Delta| = 0.01\ \mathrm{cm}^{-1}$ (0.3 GHz). In the cubic phase at $T = 160\ ^\circ\mathrm{C}$ $|a'| = 0.0017 \pm 0.0002\ \mathrm{cm}^{-1}$ (0.050 GHz), whereas in the tetragonal phase, assuming $a' = b'$, $|a'| = 0.0015\ \mathrm{cm}^{-1}$ (0.045 GHz) was determined.[31]

Note that Müller and Fayet[1] reproduced Fig. 7 $|\Delta|$ vs T of Ref. 31 with the description: "$\Delta = D(T) + a(T)$." This disagrees with the original[31] definition of $|\Delta|$, since $a(T) = a' \cdot 6$ and the approximation $a' = b'$ yields $\Delta = 2D' + a$. The values[31] of a (a') in Table (1.1) of Ref. 1 are recalculated using the incorrect Eq. (9) without realizing the inconsistent meanings of the parameters involved. Müller and Berlinger[30] quoted $a = 97 \times 10^{-4}\ \mathrm{cm}^{-1}$ (0.29 GHz) of Ref. 31 without realizing that this a (a') is not equivalent to a in Eq. (2). Decker *et al.*[21] have demonstrated the same unawareness. Conversion of: $D' = 2.7$ (Ref. 31), $a' = 0.0461$ and $b' = 0.0509$ (Ref. 21), using Eqs (14)–(16) for $S = \frac{5}{2}$ yields: $D = 2.667$, $a = 0.3054$, and $F = -0.024\,69$ (all values in GHz). These values properly reconverted to the reference notation and units are listed in Table I.

An ambiguity in recalculating the original ZFSP for Fe^{3+}:$BaTiO_3$ (tetragonal phase) to the reference notation arises from the omission of the F term in Eq. (3) by some authors. Then one must rely on some approximations. Taking $F = 0$ or $F \neq 0$ yields two alternative values of the ZFSP b_4^0, e.g., using the original data[21] (i) we can calculate F using Eq. (16) and then $b_4^0 = 24.10^{-4}\ \mathrm{cm}^{-1}$ or (ii) alternatively neglecting F we obtain $b_4^0 = 51.10^{-4}\ \mathrm{cm}^{-1}$. It turns out that neglecting F yields reasonable agreement between the ZFSPs (Ref. 21) and those reported by others (Table I). This resolves the discrepancy in question; however, it also reveals weakness of any EMR spectra analysis based on a misinterpretation of the ZFS terms. It is important to keep in mind the two distinct sources of such misinterpretations for a given symmetry: (i) omission of some operator parts leading to the nonstandard SH form[21] and (ii) neglect, due to computational reasons or low resolution of EMR spectra, of one full ZFS term, e.g., here the F tetragonal term. The latter case, with few exceptions, prevails in Fe^{3+}:$BaTiO_3$ studies.

Table I enables us to confirm the assertion[44] that a for Fe^{3+} at the Ti^{4+} sites is changing no more than 10% in all structural $BaTiO_3$ phases. Our survey reveals also some discrepancies. Rimai and deMars[46] have adopted an inappropriate relation: $a' = b_4^0$ [see Eq. (8b)] to recalculate the cubic phase ZFSP value.[31] Instead of Horning's *et al.*[31] a ($=a'$) in the cubic ($0.0017\ \mathrm{cm}^{-1}$) and tetragonal ($0.0015\ \mathrm{cm}^{-1}$) phase, only one $b_4^0 = 0.0017\ \mathrm{cm}^{-1}$ is listed[46] apparently as pertinent for both phases judging from the temperature range. The above discrepancies arise partially from the lack in the early 1960's of consistent and widely accepted ZFSP notations.

Concerning the g factors, for cubic symmetry g is isotropic, whereas two ($g_\parallel, g_\perp$) and three (g_x, g_y, g_z) components exist for tetragonal and orthorhombic symmetry. Isotropic g was mostly determined for Fe^{3+}:$BaTiO_3$ even in the noncubic phases.[27,29,33,50] This approximation is justified for $3d^5$ ions exhibiting very small g factor anisotropy. All reported g values are fairly consistent, except for the somewhat higher g, $g_\parallel$, and $g_\perp$ of Decker *et al.*[21] This may be due to either the SH used and/or the differences in computational procedure.

Comparison of the experimental (Table I) and theoretical[20] (Table II) ZFSPs indicates significant differences. In general, such differences may be induced by (i) the model of local surrounding of Fe^{3+} ions in $BaTiO_3$ adopted, (ii) the values of the microscopic parameters employed (e.g., the CF and spin-orbit coupling parameters), and (iii) intrinsic approximations/features of the theoretical method. Concerning the DFT calculations,[20] it is hard to make any meaningful comparisons without going into elaborate details. We note that the calculated[20] a and D depend strongly on the structural model, i.e., the cluster geometry. The values[20] of a are about twice lower than the experimental ones, probably due to the too weak calculated value of the cubic CF parameter Dq. The experimental values for the lac (Fe^{3+}-V_0) center $a = 102 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $D = 1.04\ \mathrm{cm}^{-1}$ (referred to as "in the rhombohedral phase") were quoted[20] from their Refs. 9 and 10, respectively. We were unable to trace down the original values in the references provided.[20]

Three structural models have been adopted[51] in the superposition model calculations of the ZFSPs for Fe^{3+}:$BaTiO_3$, each yielding different ZFSPs. The experimental data[31] yield the recalculated[51] $b_2^0 = +929\ [10^{-4}\ \mathrm{cm}^{-1}]$, as compared with the theoretically calculated using the 'Ti coordinate model' $b_2^0 = -2028\ [10^{-4}\ \mathrm{cm}^{-1}]$. Better agreement with experiment is obtained for the "centered model" considered as most accurate,[31] which yields $b_2^0 = +1047\ [10^{-4}\ \mathrm{cm}^{-1}]$, i.e., very close to the converted Hornig's *et al.* value[31] (see Table I).

TABLE I. The g factors (dimensionless) and the ZFS parameters for Fe^{3+} ions in $BaTiO_3$ reported by various authors: (i) in the original (conventional) notation and units of $[cm^{-1}]$ and (ii) converted to the reference notation b_k^q and units of $[10^{-4}\ cm^{-1}]$; for clarity the original values (OV) and spin Hamiltonian forms (OSHF) are referred to the defining equations provided in text; RT=room temperature; asterisk (*) indicates sets commented on in text.

Set	T [K]	g	D	E	a	b_2^0	b_2^2	b_4^0	b_4^4	Remarks	Ref.
					Cubic phase						
1^*	433	$g=2.003$			*0.0102 ±0.0012*			*51*	*255*	OV: $\lvert a'[\mathrm{Eq.(1b)}]\rvert=0.0017\pm0.0002\ cm^{-1}$;	31
2^*	425							17	—	OSHF: Eq. (20)	46
3^*	433	$g=2.0036$ ±0.002	≈0	≈0	0.0102 ±0.001	*≈0*	*≈0*	*51*	*255*	OSHF: Eq.(18)+Eq.(2)	33
4^*	408				0.0097			*49*	*243*	OSHF: Eq. (3) without the F term	30
5^*		$g=2.0070$ ±0.0006			*0.0090*			*45*	*225*	OV: $a'[\mathrm{Eq.(1b)}]=0.0461$ GHz=0.0015 cm^{-1}	21
					Tetragonal phase						
6^*	300	$g_\parallel=2.003$	*0.0923*		*0.0090*	*923*		*45*	*255*	OV: $\lvert a'[\mathrm{Eq.(1b)}]\rvert=0.0015\ cm^{-1}$	31
$2'^*$	300					930		17	—	OSHF: Eq. (20)	46
7^*	300	$g=2.0036$ ±0.002	0.00929	≈0	0.0091 ±0.002	*929*	≈0	*46*	*228*	OSHF: Eq.(18)+Eq.(2)	33
8	300	$g=2.003$ ±0.002	0.093		—	*930*		—	—	OSHF: Eq. (3)	34
9	RT		0.09							OSHF: Eq. (6)	29
10	RT	$g_\parallel=g_\perp$ 2.003 ±0.001	0.0991		0.0084	*991*		*42*	*210*	OSHF: Eq. (3)	45
11 *			0.094		0.0091	*940*		*46*	*228*	OSHF: Eq. (3) without the F term	20
12 *	RT	$g_\parallel=g_\perp$ =2.003 ±0.001	*0.0987 ±0.0005*		*0.0090 ±0.0002*	*987*		*45*	*225*	OV: $D=1055\pm5$ Gauss; $a^s=96\pm2$ Gauss; OSHF: Eq. (3) without the F term	43
13 *	RT	$g_\parallel=2.0070$ ±0.0006 $g_\perp=2.0096$ ±0.0006	*0.0890*		*0.0102*	*890*		*24*$^\$$ *51*$^\#$	*255* *255*	$D'[\mathrm{Eq.(1b)}]=2.7$ GHz=*0.0901* cm^{-1}; $b'[\mathrm{Eq.(1b)}]=0.0509$ GHz=*0.0017* cm^{-1}; $F=$*−0.0082* cm^{-1}; $^\$$ obtained using the value of F calculated by us; $^\#$ obtained neglecting F	21
					Orthorhombic phase						
14	213	$g=2.0036$ ±0.002	−0.064 ±0.001	$0\pm1.3\times10^{-4}$	0.0094 ±0.002	*−640*	*0 ±3.9*	*47*	*235*	OSHF: Eq. (18)+Eq. (2)	33
15	276	$g=2.0036$ ±0.002	−0.053 ±0.002	—	0.0105 ±0.002	*−530*	—	*53*	*263*	OSHF: Eq. (18)+Eq. (2)	33
					Rhombohedral phase						
16	77	$g=2.0036$ ±0.002	≈0	≈0	0.0115 ±0.001	≈0	≈0	*58*	*288*	OSHF: Eq. (18)+Eq. (2)	33
17	170	$g=2.003$ ±0.002	−0.0023 ±0.0005		—	*−23*		—	—	OV: a-$F=0.0113\pm0.001\ cm^{-1}$; OSHF: Eq. (3)	34
18	20	$g=2.005$ ±0.003	−0.0019 ±0.0005		0.0103± 0.001	*−19*		*52*	*276*	OSHF: Eq. (18)+Eq. (2)	50

Keeping in mind the inconclusive or unreliable results of the ZFSP modeling,[20,51] it would be worthwhile to carry out model calculations using the crystal field analysis (CFA) computer package,[52–54] which has recently been extended by modules enabling microscopic spin Hamiltonian (MSH) calculations.[55] The package CFA/MSH has proved to be an efficient tool for reliable modeling of the ZFSPs and g-factors for $3d^N$ ions at arbitrary symmetry sites.[56–59] The CFA/MSH computations for Fe^{3+} ions in $BaTiO_3$ are beyond the scope of this paper.

TABLE II. The theoretical ZFS parameters for Fe^{3+} ions in $BaTiO_3$ from Ref. 20: (i) in the original (conventional) notation and units of $[cm^{-1}]$ and (ii) converted to the reference notation b_k^q and units of $[10^{-4}\ cm^{-1}]$; the original labeling "lacxy" denotes the $Fe^{3+}-V_0$ centers in $BaTiO_3$; 'tetrax' stands for Fe^{3+} in tetragonal $BaTiO_3$; δ denotes the shift of the central ion position relative to the center of octahedron.

Set	D	a	b_2^0	b_4^0	b_4^4	Remarks
1	0.048	0.0033	*480*	*16.5*	*82.5*	Tetrac: $\delta_{Fe}=0$ Å; OSHF: Eq. (3) without the F term
2	0.121	0.0062	*1210*	*31*	*155*	Tetraa: $\delta_{Fe}=\delta_{Ti}=0.054$ Å; OSHF: Eq. (3) without the F term
3	0.302	0.0055	*3020*	*28*	*138*	lac0: $\delta_{Fe}=0$ Å
4	0.199	0.0030	*1990*	*15*	*75*	lac04: $\delta_{Fe}=0.4$ Å
5	0	0.0055	*0*	*28*	*138*	Cubic*; OSHF: Eq. (3) without the F term

IV. SUMMARY AND CONCLUSIONS

Reanalysis of the spin Hamiltonian (SH) forms pertinent for Fe^{3+} ions in the cubic, tetragonal, orthorhombic, and rhombohedral phase in the normal form of $BaTiO_3$ is carried out. An implicit misinterpretation of the zero-field splitting parameters (ZFSPs) used in EMR studies of $Fe^{3+}:BaTiO_3$ by Decker *et al.*[21] is revealed as responsible for a pronounced discrepancy concerning the values of the fourth-rank cubic ZFS parameter. This discrepancy is solved by reinterpretation of the ZFSPs of Decker's *et al.*[20] using the proper conversion relationships. Our considerations exemplify the pitfalls arising from the misinterpretation of the ZFPs discussed here. Comparative analysis of EMR data for $Fe^{3+}:BaTiO_3$ available in the literature is carried out. The ZFSP values for Fe^{3+} ions in various $BaTiO_3$ phases are reanalyzed, reconverted as appropriate, and tabularized in a unified way together with the g factors. Our literature survey has also revealed other inconsistencies in the SH notations occurring in EMR studies of $Fe^{3+}:BaTiO_3$, implications of which for data interpretation and compatibility have been discussed.

Two aspects beyond the scope of this paper deserve a separate study: (i) the role of other impurity ions, e.g., Fe^{2+} or Fe^{4+} and Mn^{2+} or Mn^{3+}, in EMR studies of $BaTiO_3$ and (ii) other forms of $BaTiO_3$. The EMR spectra observed in iron doped $BaTiO_3$ may be due not only to the isolated Fe^{3+} substituting for Ti^{3+} considered here, but to other centers such as Fe^{3+}-V_0 or Fe^{4+}-V_0 observed in Fe doped materials.[20,50] Another crystalline hexagonal form h-$BaTiO_3$ was investigated by EMR of Fe^{3+} ions,[22,23] yielding the low symmetry ZFSPs not directly comparable with those for the normal $BaTiO_3$ (Table I). The low symmetry aspects involved in the studies[22,23] will be considered elsewhere.[60]

This study and the complementary one[60] illustrate an importance of consistent and widely accepted conventions for the SH parameter and operator notations as well as guidelines for EMR data presentation. The present lack of such conventions and guidelines poses a serious problem for the proposed comprehensive database of the EMR-related parameters.[47,48] Straightforward entry of SH parameters extracted from source references into the database without meaningful analysis of their validity and reliability would result in proliferation of the inherent inconsistencies, such as those identified in this study. To ensure high quality of data, huge amount of work would be needed, which may be prohibitive for a small scale project. Hence, a concerted international effort in this regard seems indispensable.[47,48]

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