High-frequency electron paramagnetic resonance investigation of the Fe$^{3+}$ impurity center in polycrystalline PbTiO$_3$ in its ferroelectric phase

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The intrinsic iron(III) impurity center in polycrystalline lead titanate (PbTiO$_3$) was investigated by means of high-frequency electron paramagnetic resonance (EPR) spectroscopy in order to determine the local-environment sensitive fine structure (FS) parameter $D$. At a spectrometer frequency of 190 GHz, spectral analysis of a powder sample was unambiguously possible. The observed mean value $D = +35.28$ GHz can be rationalized if Fe$^{3+}$ ions substitute for Ti$^{4+}$ at the B-site of the perovskite ABO$_3$ lattice forming a directly coordinated Fe$^{3+}_{\text{Ti}} - V_{\text{O}}^{4-}$ defect associate. A consistent fit of the multi-frequency data necessitated use of a distribution of $D$ values with a variance of about 1 GHz. This statistical distribution of values is probably related to more distant defects and vacancies.

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I. INTRODUCTION

Lead titanate (PbTiO$_3$, PT) is widely used as functional ceramic because of its excellent physical and electromechanical properties. It is a ‘displacive-type’ ferroelectric material that can be used as dielectric in capacitors and as high refractive index thin film for electrooptical components. Its piezoelectric and pyroelectric properties can be utilized in sensors, piezoelectric actuators and detectors for infrared radiation. As compared to the solid solution lead zirconate (Pb[\text{Zr}_x\text{Ti}_{1-x}]_3\text{O}_9, PZT), lead titanate exhibits a higher Curie temperature ($T_C = 763$ K) and a lower dielectric constant of about 200, rendering it more attractive for high-temperature and high-frequency transducer applications.

In order to improve material properties, several transition metals or rare-earth elements may be added on a percentage level, for which reason considerable interest exists to characterize the role of such extrinsic functional centers. Generally, standard bulk characterization techniques fail due to the inherent low concentration of these centers and electron paramagnetic resonance (EPR) becomes the method-of-choice because of its high sensitivity and selectivity. In particular, if doping with iron is considered, the local symmetry can be explored by monitoring the resulting fine structure (FS) interaction, which will be modified by the presence of oxygen vacancies ($V_{\text{O}}^{4-}$). If charge compensation occurs in the nearest-neighbor O$^{2-}$ ion shell, a large distortion of the octahedral symmetry results and because of the short distance a large change of the intrinsic Fe$^{3+}$ FS tensor will be induced.

Unless crystalline samples are available, these tensor elements in general are not directly accessible at X-band (9.4 GHz) frequencies, since the resulting zero-field splitting (ZFS) is much larger than the microwave (mw) quantum energy. FS values therefore have to be deduced from the analysis of second-order line shifts in a fully resolved single crystal spectrum. If only powder samples are available, high-frequency EPR has to be invoked in order to approach high-field conditions, under which an accurate determination of the principal value $D$ of the FS interaction (including sign) via first-order effects is possible.

Beyond its technical importance, we can use lead titanate as a model system related to the considerably more complex acceptor-doped PZT systems, because its structure being comparatively simple and well defined. Furthermore, a prerequisite for an analysis of the EPR spectra of solid-solution PZT systems with varying Pb/Zr composition is a complete characterization of the spectra of pure compounds. As stated above, in general it is quite difficult to extract large ZFS tensor elements from X-band EPR powder spectra. In order to establish high-frequency EPR as reliable tool for the investigation of technologically relevant polycrystalline compounds, we have chosen the ubiquitous Fe$^{3+}$ impurity center in lead titanate powder as first example, because FS parameters have been obtained by previous single crystal studies which can be used for comparison.

The first EPR spectrum, attributed to Fe$^{3+}$ in PbTiO$_3$ led to the discovery of an unusual high FS splitting. This observation was related to the strong tetragonal ferroelectric distortion of the crystalline field. At Q-band (35 GHz), two different iron centers were observed, one of them being assigned to a partially charge-compensated Fe$^{3+}_{\text{Ti}} - V_{\text{O}}^{4-}$ defect associate. It was also observed that the
FS interaction increases by 20% when cooling from room temperature to 77 K, consistent with a change in lattice deformation, the $c/a$ ratio changing by 19% in this temperature range. The spectra allowed also for the determination of additional terms attributed to higher-rank tensor elements. The temperature dependence of line intensities at liquid helium temperatures indicated that the sign of $D$ is positive. At 70 GHz, additional transitions could be observed and allowed to refine the ZFS parameters. In contrast to these findings, in a recent X-band EPR study only a single Fe$^{3+}$ center was observed, for which charge compensation was assumed to occur at distant spheres. This discrepancy was attributed to different synthesis techniques involved in manufacturing the crystals. At low temperatures hyperfine structure, assigned to interaction with nearby $^{207}$Pb nuclei was observed.

The reported ZFS parameters are spread over a broad range. Since many attempts for gaining structural information about the dopant site, such as the assignment to either Fe$^{3+}_{V^{-}}$ or Fe$^{3+}_{V^{+}}$ defect associates or not-coordinated ‘free’ Fe$^{3+}_{Ti}$ centers with or without off-center shifts of the iron ion, are based upon size and sign of the ZFS parameters, their precise determination is of considerable importance. By taking the reported interval of ZFS parameters as input parameters for modelling the structure of the iron center, a contradictory variety of proposed structures results, ranging from ‘free’ Fe$^{3+}_{Ti}$ centers to Fe$^{3+}_{Ti}$ – Fe$^{3+}_{O}$ defect associates with off-center shifts towards or away from the oxygen vacancy. In this work, we hence aim for an unambiguous determination of the ZFS parameter by application of high-frequency EPR up to 190 GHz, thus creating the basis for an accurate modelling of the structure. In the magnetic field range of 2 to 8 T used, the electron Zeeman energy will be the dominant term in the spin Hamiltonian. Resulting quantization approximately along the field direction significantly simplifies the EPR spectrum. Accordingly it is possible to accurately determine ZFS parameters of Fe$^{3+}$ in polycrystalline PbTiO$_3$ from observed van Hove singularities, which are related to canonical orientations of the compound. High frequency EPR thus is an indispensable tool for the investigation of technologically relevant PZT, which are commonly available only as disordered compounds.

II. EXPERIMENTAL

9.5 GHz continuous wave (c.w.) EPR measurements were performed using an ESP 300E spectrometer (Bruker), equipped with a rectangular TE$_{112}$ resonator. The magnetic field was read out with a NMR gaussmeter (ER 035M, Bruker) and as a standard field marker polycrystalline DPPH with $g = 2.0036$ was used for the exact determination of the resonance magnetic field values. High-frequency EPR measurements were performed at the National High Magnetic Field Laboratory (NHMFL) Tallahassee. The set-up used operates in transmission mode and employs oversized cylindrical wave guides. No resonator was used. Microwave detection was performed with a low-noise, fast response InSb hot-electron bolometer (QMC Ltd.), operated at liquid-helium temperature. Field modulation in the range of 10 to 50 kHz was used to obtain ‘first-derivative’ type EPR spectra.

III. THEORETICAL DESCRIPTION

In principle, a discussion of the Fe$^{3+}$ center in its high-spin form ($S = \frac{5}{2}$) should be based upon the most general form of the spin Hamiltonian, including fourth-rank tensor components. However, literature values of spin-Hamiltonian parameters for Fe$^{3+}$ ions in lead titanate single crystals, as well as our high-field EPR results justify considerable simplifications. First, since no significant line broadening was observed in high magnetic fields, the anisotropy of the $g$-matrix apparently imposes a much smaller angular-dependent EPR resonance shifts than the inherent peak-to-peak linewidth $\Delta B_{pp}$ of the resonance lines and might therefore be neglected. This is in agreement with expectation because of a vanishing orbital momentum of Fe$^{3+}$ ions. As a consequence, the electron Zeeman interaction will be represented by an isotropic $g$-value. Second, due to the relatively low natural abundance of the only magnetic active isotope,$^{57}$Fe iron hyperfine interaction will be omitted for spectrum reconstruction. Third, the nuclear Zeeman interaction is ignored as well because it does not contribute to EPR spectral features in first order. Finally, no influence of fourth-rank tensor elements could be experimentally resolved. Hence, the corresponding terms were neglected.

The resulting simplified effective spin Hamiltonian is given by

$$\mathcal{H} = S \cdot D \cdot S + g_{iso} \beta \cdot B_{0} \cdot S$$

(1)

in which $g_{iso}$, $g_{n}$ are the electron and nuclear $g$ factors and $\beta_e$, $\beta_n$ are the Bohr and nuclear magnetons. The second and third terms are the electronic and nuclear Zeeman interactions, respectively, and $B_{0}$ is denoting the external field. The first term describes the second-rank fine structure interaction. This term is often referred to as the zero-field splitting term because it lifts the degeneracy of energy states independent of magnetic field. The FS tensor $D$ is symmetric and traceless. Thus, there is always a coordinate system in which the tensor is diagonal with the elements $D_{||}$ and $D_{\perp}$. By convention, $D_{||}$ is taken to be the principal value with the largest absolute magnitude. Hence, for axial symmetry, the fine-structure splitting may be described in terms of a single crystal-field parameter that is commonly defined as $D = \frac{3}{2}D_{||} = 3D_{\perp}$. The free Fe$^{3+}$ ion has a $3d^{5}$ $^6S_{5/2}$ ground state. Under the action of a tetragonal crystalline field, this ground state splits into three twofold degenerate levels (cf. figure 1(b)).
In case of the commonly employed X-band frequencies, the zero-field splitting is much larger than the electron Zeeman energy. All doublets are well separated and only transitions within each doublet can be observed. Accordingly, the spectrum then is described by defining a separate effective spin Hamiltonian with $S' = \frac{1}{2}$ for each doublet. Because of orientation-dependent state mixing, the effective $g'$-matrices can exhibit a very large anisotropy even retaining the assumption that the pure electron Zeeman interaction is isotropic. This situation is schematically represented in figure 1(a, c). At zero field, the spins are quantized along the $z$-axis and the degeneracy being lifted proportional to $B_0$. However, due to the zero-field splitting being larger than the mw quantum of energy at X-band frequencies, only transitions between levels degenerate at zero field may be induced, providing such transitions are not 'forbidden' by the selection rule $\Delta m_S = \pm 1$. If the magnetic field is perpendicular to the $z$-axis, there is no first-order splitting of the $|m_S = \pm \frac{1}{2}\rangle$ and $|\pm \frac{3}{2}\rangle$ states, whereas the $|\pm \frac{1}{2}\rangle$ states are split with $g' \approx 6$. Due to the selection rule all transitions, except the $|m_S = +\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ transition are 'forbidden' and will not be observed in the X-band EPR spectrum.

IV. RESULTS AND DISCUSSION

A typical X-band EPR spectrum is presented in figure 1(b). It mainly consists of one prominent feature at low field. In terms of effective $g$-values, the spectrum is described with $g'_\parallel = 2.004$ and $g'_\perp = 5.956$. Because all orientations are statistically realized in a powder, the resonances extend from $g'_\parallel$ to $g'_\perp$, as illustrated in figure 1(c), and because the probability of $B_0$ being perpendicular to the $z$-axis is largest, the resonance peak at $g'_\perp$ is the dominant feature. The additional feature at $g = 2.2$ can be assigned to Pb$^{3+}$ centers.

The W-band EPR spectrum (95 GHz), depicted in figure 2(a), is representative for an intermediate field regime. For this situation the crystal-field terms are comparable to the electron Zeeman interaction. Hence, no simple prediction pattern of the EPR spectrum results. The observed sharp lines, however, can be identified as arising from to resonances with minor orientation dependence, as shown in figure 2(b). To obtain good agreement between simulation and experiment, it had to be assumed that the sample was exposed to oscillating $B_1$ field components being both parallel and perpendicular to $B_0$. This phenomenon is caused by multiple reflections and general imperfections (mode impurity) in the mw propagation system, in contrast to cavity-based systems with a well-defined $B_1$ polarization. For spectrum simulations this effect necessitates consideration of parallel and perpendicular EPR modes. In the perpendicular mode, the excitation and detection mw fields are along the laboratory $x$-axis, whereas in the parallel mode they are along the $z$-axis, parallel to the external static field. When the magnetic field is parallel to a principal axis, the EPR $\Delta m_S = \pm 2$ transition probability drops to zero with the modulation field $B_1$ perpendicular to $B_0$, while it is largest with $B_1$ parallel to $B_0$, enabling the observation of 'forbidden' transitions.

At G-band (190 GHz), EPR is performed almost in the high-field regime. The corresponding energy-level diagrams for the canonical orientation perpendicular relat-
Figure 2: (a) W-band EPR spectrum of the Fe$^{3+}$ impurity center in PbTiO$_3$ at $\nu_{mw} = 95.284$ GHz (T = 10 K). Numerical spectrum simulations involve $B_1$ in perpendicular (top) and parallel (bottom) mode. (b) Orientation dependence of EPR transitions.

Figure 3: (a) G-band EPR spectrum of the Fe$^{3+}$ impurity center in PbTiO$_3$ at $\nu_{mw} = 189.962$ GHz and T = 10 K (iii). Numerical spectrum simulations involve both $B_1$ in perpendicular (i,ii) and parallel (iv,v) mode, as well as a positive (solid) and negative sign (dashed) of the axial ZFS parameter. The transition being particularly sensitive to temperature-dependent level population is marked by an asterisk. (b) Energy levels as function of magnetic field for the canonical parallel (left) and perpendicular (right) orientations relative to the ZFS-tensor principal axes using $D > 0$. EPR transitions for G-band frequencies are marked by vertical lines involving 'allowed' (solid) and 'forbidden' transitions (dashed).

The refinement of the spin-Hamiltonian parameters through numerical spectrum simulation simultaneously for all mw frequencies led to the results summarized in table I. Using these best-fit values, numerically simulated spectra are superimposed to the experimental data and show excellent agreement. Concerning the relatively large value of $D$, the local environment for the Fe$^{3+}$ ion can be modelled with the help of the semi-empirical Newman superposition model$^{19}$. The geometry of the next-nearest oxygen positions was calculated using the lattice parameters $c = 0.422$ nm and $a = 0.386$ nm from XAFS measurements at 12 K$^{20}$. The parameters for the iron-oxygen ion pair were taken as $R_2 = -12.36$ GHz at a reference distance of $R_0 = 0.2101$ nm, and the power-law exponent as $t_2 = 8^{21}$, respectively. Only by assuming Fe$^{3+}$ being located at the B-site correlated with a next-nearest oxygen vacancy, the measured value for the ZFS could be reproduced within the centered mode$^{22}$. An
Table I: Table I: $g$-values and FS parameters as obtained from high-field EPR, compared to values from literature with $\nu_{mw}$. The sign of the principal ZFS parameter is determined by an analysis of line intensities at low temperatures. (For a definition of the fourth-order parameters $a, F$ see for example: A. Abragam, B. Bleaney: *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford (1970))

| center     | $g_{iso}$ | $D$ [GHz] | $a$ [MHz] | $F$ [MHz] | $T$ [K] | $\nu_{mw}$ [GHz] |
|------------|-----------|-----------|-----------|-----------|--------|------------------|
| Fe$^\prime$ - V$_O^{\prime\prime}$ | 2.002     | 35.28 ± 0.01 | 1678 ± 10 | 2833 ± 10 | 290   | 9.6 - 190         |
| Fe$^\prime$ | 2.009(5)  | 27.13 ± 0.01 | 32 ± 1    | 1678 ± 10 | 290   | 9.4              |
| Fe$^\prime$ - V$_O^{\prime}$ | 35.59 ± 0.06 | 600 ± 210 | 510 ± 300 | 85       | 70    |                  |
| Fe$^\prime$ | 34.48 ± 0.09 | 660 ± 300 | 600 ± 300 | 77       |       |                  |
| Fe$^\prime$ - V$_O^{\prime\prime}$ | 26.98 ± 1.5 | 809 ± 120 |            | 77       |       |                  |
| Fe$^\prime$ | 15.89 ± 0.1  | 809 ± 120 |            | 290      | 37.5  |                  |
| Fe$^\prime$ - V$_O^{\prime\prime}$ | 32.98 ± 1.5 | 809 ± 120 |            | 77       |       |                  |
| Fe$^\prime$ | 20.08 ± 0.6  | 809 ± 120 |            | 290      | 37.5  |                  |
| Fe$^\prime$ | 2.009(5)     | 2.0       | ≥ 30       | 9.4      |       |                  |

off-center displacement of the iron in an intact oxygen octahedron leads to a considerably smaller value ($D \leq 25$ GHz). Based upon the experimentally determined FS value, the conclusion is thus drawn that iron builds a defect associate with a directly coordinated oxygen vacancy (Fe$^\prime$$_{T_1}$ - V$_O^{\prime\prime}$). These results are in agreement with predictions obtained by ab-initio calculations, which are in progress.

Moreover, it can be concluded from the axial symmetry of the ZFS tensor that the orientation of the Fe$^\prime$$_{T_1}$ - V$_O^{\prime\prime}$ defect dipole is along the crystallographic c-axis. Any other coordination of the oxygen vacancy along either a or b would reduce the symmetry of the ZFS tensor to orthorhombic, which was not observed within spectral resolution.

Starting with $D$ as a single fit parameter, a satisfactory reproduction of the experimental data taken at all different mw frequencies was possible only when allowing for statistical Gaussian distributions $\delta D$. Considering the inhomogeneous charge-compensation mechanisms, provided by either lead vacancies (V$^{\prime\prime}_{Pb}$) or valency-altered Pb$^{3+}$ centers, and considering that these defects can be in different shells of the Fe$^\prime$$_{T_1}$ - V$_O^{\prime\prime}$ defect associate, a statistical distribution (strain) of the spin-Hamiltonian parameters defined by corresponding variances is expected. In our case, a variance $\delta D = 1$ GHz of the ZFS parameter $D$, taken to be Gaussian and independent over the mw frequency range from 9.6 to 94 GHz, had to be assumed.

The high-field approach thus allows for determining absolute value and sign of the axial fine structure parameter for polycrystalline compounds without ambiguity and even superior accuracy as compared to single crystal studies at X-band frequencies. This is due to the fact that FS values at high fields can accurately be determined via first-order effects rather than by second-order shifts at low fields. A second consequence is that a distribution $\delta D$ of the FS parameter is observable as first-order variation of the line positions that result in line broadening in the high-field spectra. At X-band, this effect is of second-order only and thus almost vanishes. Hence no information about $D$-strain can be gathered. In contrast, fourth order FS parameters were not accessible by numerical spectrum simulations up to 190 GHz, which in turn are accessible by orientation-dependent single-crystal studies at X-band.

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1. B. Jaffe, W.R. Cook, H. Jaffe: *Piezoelectric ceramics*, Academic Press, London (1971)
2. Y. Xu: *Ferroelectric materials and their applications*, Elsevier, Amsterdam (1991)
3. K. Uchino: *Ferroelectric devices*, Dekker Inc., New York (2000)
4. M.E. Lines, A.M. Glass: *Principles and applications of ferroelectrics and related materials*, Oxford University Press, Oxford (2001)
5. (a) R.-A. Eichel, H. Kungl, M.J. Hoffmann, J. Appl. Phys. 95 (2004) 8092-8096; (b) R.-A. Eichel, K.-P. Dinse, H. Kungl, M.J. Hoffmann, A. Ozarowski, J. van Tol, L.C.
6 (a) D. Hennings, H. Pomplun, J. Am. Ceram. Soc. 57 (1974) 527-530; (b) R. Böttcher, W. Brunner, B. Milsch, G. Völkel, W. Windsch, S.T. Kirillov, Chem. Phys. Lett. 129 (1986) 546-549; (c) R. Heidler, W. Windsch, R. Böttcher, C. Klimm, Chem. Phys. Lett. 175 (1990) 55-58; (d) G. Klotzsche, W. Windsch, W. Wojcik, Ferroelectrics Lett. Sect. 15 (1993) 115-120; (e) O. Bidault, M. Actis, M. Maglione, Solid State Commun. 95 (1995) 845-849; (f) D.J. Keeble, Z. Li, M. Harmatz, J. Phys. Chem. Solids 57 (1996) 1513-1515; (g) D.J. Keeble, E.H. Poindexter, G.J. Gerard, Appl. Spectroscopy 51 (1997) 117-122; (h) W.L. Warren, B.A. Tuttle, B.N. Sun, Y. Huang, D.A. Payne, Appl. Phys. Lett. 62 (1993) 146-148; (i) P.G. Clem, W.L. Warren, J. Appl. Phys. 77 (1995) 5865-5868; (j) V.V. Laguta, T.V. Antimirova, M.D. Glinchuk, I.P. Bykov, J. Rosa, M. Zaritskii, L. Jastrabik, J. Phys.: Condens. Matter 9 (1997) 10041-10049; (j) J. Huang, N.D. Chasteen, J.J. Fitzgerald, Chem. Mater. 10 (1998) 3848-3855; (k) K. Hayashi, A. Ando, Y. Hamaji, Y. Sakabe, Jpn. J. Appl. Phys. 37 (1998) 5237-5240; (l) E. Erdem, R. Böttcher, H.C. Semmelhack, H.J. Glass, E. Hartmann, phys. stat. sol. B 239 (2003) R7-R9

7 The Kröger and Vink notation is used to describe the charge state of the defect with respect to the neutral lattice.

8 Intrinsic’ in this context refers to the fact that the B-site symmetry in the ferroelectric phase already allows the existence of an axial FS tensor even without the presence of oxygen vacancies.

9 D.J.A. Gainon, Phys. Rev. 134 (1964) A1300-A1301
10 R.G. Pontin, E.F. Slade, D.J.E. Ingram, J. Phys. C 2 (1969) 1146
11 O. Lewis, G. Wessel, Phys. Rev. B 13 (1976) 2742-2746
12 V.V. Laguta, M.D. Glinchuk, I.P. Bykov, Y.L. Maksimenko, J. Rosa, L. Jastrabik, Phys. Rev. B 54 (1996) 12353-12360
13 A.K. Hassan, L.A. Pardi, J. Krzystek, A. Sienkiewicz, P. Goy, M. Rohrer, L.C. Brunel, J. Magn. Reson. 142 (2000) 300-312
14 A. Abragam, B. Bleaney: Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford (1970)
15 (a) J.S. Griffith, Biopolymer. 1 (1964) 35; (b) H.H. Wicke, M.P. Klein, D.A. Shirley, J. Chem. Phys. 42 (1965) 2113; (c) W.T. Oosterhuis, Struct. Bond. 20 (1974) 19; (d) J.R. Pilbrow, J. Magn. Reson. 31 (1978) 479-490
16 J. Krzystek, S.A. Zvyagin, A. Ozarowski, A.T. Fiedler, T.C. Brunold, J. Telser, J. Am. Chem. Soc. 126 (2004) 2148-2155
17 (a) Bruker Xsophe Simulation Package v.1.1.3; (b) EasySpin EPR toolbox v.2.0.3, ETH Zürich
18 J. Krzystek, S.A. Zvyagin, A. Ozarowski, A.T. Fiedler, T.C. Brunold, J. Telser, J. Am. Chem. Soc. 126 (2004) 2148-2155
19 D.J. Newman and B. Ng, Rep. Prog. Phys. 52 (1989) 699
20 N. Sircon, B. Ravel, Y. Yacoby, E.A. Stern, F. Dogan and J.J. Rehr, Phys. Rev. B 50 (1994) 13168
21 E. Siegel and K.A. Müller, Phys. Rev. B 19 (1979) 109
22 E. Siegel and K.A. Müller, Phys. Rev. B 20 (1979) 3587
23 So. Laubach, St. Laubach, P.C. Schmidt, private communication