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Local position of Fe$^{3+}$ in ferroelectric BaTiO$_3$

E. Siegel, K. A. Müller (*)
Institut für Angewandte Physik, Universität Bonn, 5300 Bonn 1, West Germany

Résumé. — Le spectre R.P.E. du Fe$^{3+}$ dans les trois phases ferroélectriques du BaTiO$_3$ peut être interprété sur le principe de superposition du modèle de Newman. Dans ce cas, la position des ligands les plus proches détermine le spectre R.P.E. Nous avons trouvé que le Fe$^{3+}$ participe moins au mouvement collectif que les ions Ti$^{4+}$. Si nous admettons que Fe$^{3+}$ se trouve au centre d’un octaèdre et que nous prenons les coordonnées de l’oxygène et les paramètres intrinsèques du modèle de Newman, nous pouvons obtenir le signe et la grandeur des termes $b_2^i$ R.P.E. Si Fe$^{3+}$ se trouve au centre nous obtenons aussi des paramètres justes $b_2^i$ du PbTiO$_3$ et KNbO$_3$. L’étude a montré que Fe$^{3+}$ est très sensible aux positions intrinsèques de l’oxygène. La configuration 3d$^5$ du Fe$^{3+}$ semble jouer un rôle sur la répression de la ferro-électricité.

Abstract. — The EPR spectra of Fe$^{3+}$ in the three ferroelectric phases of BaTiO$_3$ could be interpreted on the basis of the Newman superposition model. In the latter, the position of the nearest (oxygen) ligands determines the EPR spectrum. It is found that the Fe$^{3+}$ participates by less than an order of magnitude in the collective motion of the Ti$^{4+}$ ions out of their inversion symmetric position: by centering the Fe$^{3+}$ and using previously determined intrinsic oxygen coordinates and parameters of the Newman model, the sign and magnitude of the EPR $b_2^i$ terms could be obtained. The centered Fe$^{3+}$ also yields correct EPR $b_2^i$ parameters for PbTiO$_3$ and KNbO$_3$. The investigation shows that the Fe$^{3+}$ is a very sensitive probe of the intrinsic oxygen positions. The small coupling of the Fe$^{3+}$ to the off-center ferroelectric motion is ascribed to its half-filled 3d shell.

1. Introduction. — BaTiO$_3$ is one of the best-known displacive ferroelectric systems. It belongs to the perovskite structure and has three phase transitions, from cubic to tetragonal, tetragonal to orthorhombic and orthorhombic to rhombohedral. The first complete study of Fe$^{3+}$ in the tetragonal phase was carried out by Hornig, Rempel and Weaver using c-domain crystals [1]. Subsequent studies by Sakudo [2] and Sakudo and Unoki [2] extended the investigations to the orthorhombic Amm2 and rhombohedral R3m phases. The main results of these papers are:

(i) The local symmetry of Fe$^{3+}$ in the cubic and tetragonal phases reflects the symmetry of the bulk material [1].

(ii) In the orthorhombic phase, the EPR spectrum does not show the orthorhombicity of the bulk material. The local symmetry is tetragonal, with its axis parallel to a cubic $\langle 100 \rangle$ axis perpendicular to the spontaneous $\langle 110 \rangle$ polarization [2].

(iii) In the rhombohedral phase, the axial splitting parameter $b_2^i$ was found to be more than an order of magnitude smaller than in the orthorhombic and tetragonal phases; contrary to expectations, since in all three phases the spontaneous Ti displacement and the polarizations are of the same order of magnitude [2, 3].

The aim of this investigation was to give an understanding of the unexpected behavior of Fe$^{3+}$ in BaTiO$_3$, which has not been clarified till now. The analytic basis of this understanding is the superposition model of Newman [4] reviewed by Newman and Urban [5]. Owing to the latest success of this model in the interpretation of the Fe$^{3+}$ EPR data, it is now possible to obtain detailed information on the local surroundings of the Fe$^{3+}$ ion as demonstrated by Siegel and Müller [6].

2. Model calculations. — In the superposition model the essential equation, which correlates the EPR parameters $b_2^i$ and $b_3^i$ with the surroundings of the paramagnetic ion is

$$b_2^i = 2(R_0) \sum_{i=1}^{N} \left( \frac{R_i}{R_0} \right)^{1/2} K_2^i(\theta_i, \Phi_i)$$

where $R_0 = 2.10$ Å is a reference distance, $R_i$, $\theta_i$, $\Phi_i$ the distance and angles to the $i$th ligand,

$$K_2^i(\theta, \Phi) = \frac{1}{2}(3 \cos^2 \theta - 1) \ ,$$

$$K_2^i(\theta, \Phi) = \frac{3}{2} \sin^2 \theta \cos 2 \Phi \ ,$$

$\tilde{b}_2(2.10 \text{ Å}) = -0.412(25) \text{ cm}^{-1}$ and $t_2 = 8 \pm 1$

are the intrinsic parameters for Fe$^{3+}$-$O$ ligands determined previously [6, 7].

In the substitutional model we assumed that Fe$^{3+}$ is on the Ti$^{4+}$ site with ionic coordinates identical to...
Ti$^{4+}$. This model corresponds to the assumptions normally made in EPR. The local surroundings of Fe$^{3+}$ consist of an oxygen octahedron distorted in the tetragonal, orthorhombic and rhombohedral phases. The results for the three phases of BaTiO$_3$ are given in Table I, where the experimental values are shown in the first column. In the second, the calculated values for the Ti coordinate model are presented. A comparison shows that three fundamental discrepancies exist.

(i) The calculated signs of $b_3^2$ in the tetragonal, orthorhombic and rhombohedral phases are opposite to the measured signs.

(ii) The calculated value of $b_2^2$ in the orthorhombic phase is large, whereas the measured value of $b_2^2$ is zero within the experimental error limit.

(iii) In the rhombohedral phase, the calculated value shows a strong axiality comparable to the tetragonal and orthorhombic phases, which is not found experimentally.

From these three discrepancies, we conclude that Fe$^{3+}$ does not have ionic coordinates identical to Ti$^{4+}$. Thus Fe$^{3+}$ behaves differently from Ti$^{4+}$.

In the one-parameter model, we therefore assumed that Fe$^{3+}$ deviates from the exact crystallographic position. This deviation is described by a displacement $\Delta$, which is parametrized in units of the lattice constants. The displacement is assumed to be in the direction of the polarization in each phase. For a given value of $\Delta$ the distances and angles were calculated and with eq. (1), $b_2^2$ and $b_3^2$ were determined. By this one-parameter model, which only varies the Fe$^{3+}$ position and takes the oxygens on the ideal crystallographic position, all measured amounts and signs of $b_2^2$ or $b_3^2$ in BaTiO$_3$ can be explained for one specific chosen value of $\Delta$ in each phase summarized in Table I [8]. Comparing the $\Delta$ values of Table I ($|\Delta| \approx 0.02$) with the crystallographic oxygen shift data in the tetragonal, orthorhombic and rhombohedral phases, they are found to be quite similar. This means that the Fe$^{3+}$ has about the same deviation from the ideal crystallographic Ti$^{4+}$ position as the shift of the oxygens in all phases of BaTiO$_3$ through any of their phase transitions. Therefore Fe$^{3+}$ is sited near the center of the octahedron. Considering now that the octahedron is immobile, then the Ti$^{4+}$ ion is at the center of the octahedron in the cubic phase, and shifts off-center by about 0.1 Å along the <100>, <110> or <111> directions in the tetragonal, orthorhombic and rhombohedral phases. However, Fe$^{3+}$ remains, according to our results, in all phases near the center of the octahedron.

We took this result as the starting point for the centered model which assumes: (i) Fe$^{3+}$ is at the center of the octahedron. (ii) The distortions in the oxygen octahedron surrounding Fe$^{3+}$ will be caused only through changes in the lattice constants. Using the crystallographic data [8], the EPR parameters in Table I of the last column were obtained.

The calculated sign of $b_2^2$ is identical with the measured sign in all three ferroelectric phases. The amounts of $b_3^2$ in the tetragonal and orthorhombic phases can be predicted very well. The calculated value of $b_2^2$ is very small compared to that of the Ti coordinate model. The error of $b_2^2$ given in Table I originated only from the error in the lattice constants and from the error in $b_2$.

In the rhombohedral phase, the parameter $b_2^2$ is 20 times smaller than in the Ti coordinate model. It also has the correct order of magnitude. The error given here comes from the assumed error in the rhombohedral angle $\gamma$ of 0.02° and that of $b_2$. The main result of this model is that all the experimental $b_2^2$, $b_3^2$ data of BaTiO$_3$ can be explained sufficiently in centering the Fe$^{3+}$ and taking the intrinsic oxygen coordinates.

Fe$^{3+}$ in PbTiO$_3$ and KNbO$_3$: There are only a few oxide perovskites, apart from BaTiO$_3$ and SrTiO$_3$, with known Fe$^{3+}$ EPR data. Therefore, with the same models as for BaTiO$_3$, the PbTiO$_3$ and KNbO$_3$ compounds were investigated. In Table II all relevant EPR data for Fe$^{3+}$ in PbTiO$_3$ [9] and KNbO$_3$ [10] are given.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Experimental EPR data $[10^{-4}$ cm$^{-1}]$</th>
<th>Ti coordinate model $[10^{-4}$ cm$^{-1}]$</th>
<th>One-parameter model deviation $\Delta$</th>
<th>Centered model $[10^{-4}$ cm$^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal phase</td>
<td>$b_3^2 = +929$ at $T = 300$ K Ref. [1]</td>
<td>$b_2^2 = -2028 (700)$</td>
<td>$\Delta \approx -0.03$</td>
<td>$b_2^2 = +1047 (250)$</td>
</tr>
<tr>
<td>Orthorhombic (*)</td>
<td>$b_3^2 = -530 (10)$ at $T = 276$ K Ref. [2]</td>
<td>$b_2^2 = +760 (300)$</td>
<td>$\Delta \approx -0.02$</td>
<td>$b_2^2 = -565 (136)$</td>
</tr>
<tr>
<td></td>
<td>$b_2^2 = 0$</td>
<td>$b_2^2 = +1245 (300)$</td>
<td>$\Delta \approx +0.02$</td>
<td>$b_2^2 = -82 (22)$</td>
</tr>
<tr>
<td>Rhombohedral phase</td>
<td>$b_3^2 = -23 (5)$ at $T = 173$ K Ref. [3]</td>
<td>$b_2^2 = +1585 (400)$</td>
<td></td>
<td>$b_2^2 = -83 (19)$</td>
</tr>
</tbody>
</table>

(*) EPR main axis along a <100> axis.
The remarkable features of tetragonal PbTiO$_3$ are: the Ti coordinate model predicts the wrong sign of $b_2^q$, therefore Fe$^{3+}$ has ionic coordinates different from Ti$^{4+}$. On the other hand, the centered model predicts correctly the sign and magnitude of the experimental EPR data. Therefore Fe$^{3+}$ in PbTiO$_3$ behaves in the same manner as Fe$^{3+}$ in BaTiO$_3$. For KNbO$_3$, only EPR data for the orthorhombic phase are known without the knowledge of the signs of $b_2^q$ and $b_2^q$. From comparison with the orthorhombic phase of BaTiO$_3$, one would expect a negative sign of $b_2^q$. In the Nb coordinate model, the calculated $b_2^q$ parameter is of an order of magnitude too large, therefore the ratio $b_2^q/b_2^q$ is also too large compared with the experimental value. In the centered model, the value of $b_2^q$ and also the correct order of magnitude of $b_2^q$ can be successfully predicted. These two compounds show that the behavior of Fe$^{3+}$ in BaTiO$_3$ is not an exception but rather a more common feature than expected.

A corresponding analysis was also carried out for the Mn$^{2+}$ EPR data of tetragonal BaTiO$_3$ and PbTiO$_3$ [8]. The main results are: (i) Mn$^{2+}$ does not have identical coordinates like Ti$^{4+}$ in these ferroelectric oxide perovskites either; (ii) the directions of the displacement of the Fe$^{3+}$ and Mn$^{2+}$ ions are the same, and (iii) the positions of Fe$^{3+}$ and Mn$^{2+}$ are different in these compounds probably due to the difference in the nominal charge and the sizable differences in the ionic radii

$$[r(\text{Mn}^{2+}) - r(\text{Ti}^{4+}) = 0.23 \text{ Å}]$$


3. Discussion. — The superposition model shows that Fe$^{3+}$ in ferroelectric BaTiO$_3$ does not have ionic coordinates identical to Ti$^{4+}$. It is in the center of the octahedron. The Fe$^{3+}$ ion, therefore, does not move out of the inversion symmetric position as the Ti$^{4+}$ does. Fe$^{3+}$ is passive and does not take part in the phase transitions as the Ti$^{4+}$ does. However, it sees the near intrinsic oxygen surrounding and therefore

is a very useful probe about the bulk oxygen lattice alone. This behavior of Fe$^{3+}$ in BaTiO$_3$ is not a single example, but rather appears to be a general feature in ferroelectric oxide perovskites as our results in PbTiO$_3$ and KNbO$_3$ indicate. The larger Mn$^{2+}$ behaves in a similar but not identical manner.

Our microscopic findings on the local position of the Fe$^{3+}$ in BaTiO$_3$ is also of value to understand the shift in $T_c$ upon iron doping. The spontaneous polarization of the ferroelectric BaTiO$_3$ stems mainly from the shift of the Ti$^{4+}$ ions from the center of the oxygen octahedra. In Fe$^{3+}$ doped BaTiO$_3$, the local polarization in a Fe$^{3+}$O$_6$ cluster is zero because Fe$^{3+}$ is in the center of the octahedron. Therefore, the polarization of the entire material is reduced proportionally to the concentration of the doping. The dipole-dipole interaction between the permanent dipoles is also partly blocked, and the region of correlation will be smaller than in undoped material. $T_c$ will therefore be reduced by doping with Fe$^{3+}$. This characteristic behavior was observed by Arend [12] and more recently by Ihrig [13] for the cubic-to-tetragonal phase transition of BaTiO$_3$ of $-20 \text{ K}$ per mole $\%$ of Fe$^{3+}$ content.

Arguments of lattice dynamical theories and shell models make it improbable that the small differences in the mass of Ti versus Fe or their effective charge are responsible for the different behavior [8]. However the Fe$^{3+}$ has a half-filled 3d shell, 3$d^5$, as the Sn$^{4+}$ has a completely-filled 4d shell, 4$d^{10}$, i.e., their anti- and non-bonding d orbitals are half or totally occupied. Both ions suppress the ferroelectric transition [14] and have about the same size [9]. Thus the unfilled d shells of Ti$^{4+}$ and Nb$^{5+}$ appear to be crucial to the existence of ferroelectricity with displaced B ions, apart from the anisotropic nonlinear polarizability of the oxygens (absent for $S^2-$, $F^-$, $Cl^-$, etc.). If the latter p electron charge can move onto empty d cation orbits, the oxygen shell polarizability is enhanced and ferroelectricity occurs. Here we have certain evidence that a half-occupied d shell is sufficient to inhibit the effect.
DISCUSSION

Question. — O. Schirmer.

Apparently, the low-charged defects are moving less off-centre than those of higher charge. Therefore, one expects lower coupling to the surrounding polarisation in the former case. Is this a possible explanation?

Reply. — E. Siegel.

For Fe³⁺ and Mn²⁺ this would be a possible explanation but two points make this interpretation doubtful: (i) In these compounds these ions have effective charges, which differ considerably from the nominal charge; (ii) Sn⁴⁺ with a nominal charge identical to Ti⁴⁺ suppresses also the phase transition. (BaSnO₃ is not ferroelectric.)

References

[8] A detailed account of the present investigation.