# INTERPRETATION OF THE CHANGE IN HALF-LIFE
## OF $^{89}$Zr IN BaTi(Zr)O$_3$ AT THE UPPER PHASE TRANSITION
### ($T_c$ = 120°C)

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**Synopsis**

An attempt was made to explain the change in the decay constant of $^{89}$Zr in BaTi(Zr)O$_3$ at the upper phase transition ($T_c$ = 120°C) by the change of the ligand field. A theoretical estimate of the change in half-life is given.

1. *Introduction.* A change in half-life of $^{89}$Zr at the site of the Ti ion in BaTiO$_3$ at the upper phase transition ($T_c$ = 120°C) was observed[1,2]. Recently an analogous experiment was performed by Nishi *et al.*[3] with the isotope $^{99}$Tc$^m$. Both experiments indicate a change in half-life, when the crystal undergoes the phase transition at $T_c$ = 120°C. With $^{89}$Zr a relative change in the decay constant $\Delta\lambda/\lambda$ = (8.0 ± 0.3) × 10$^{-4}$ was observed[2]. This change can be interpreted by a change in the electron density at the Zr nucleus, which is the consequence of a change in the character of the chemical bonding or the ligand field. For the actual estimate of the alteration in electron density the perturbation calculation of Bloembergen and Dixon[4] was used, introducing a "ferroelectric field" $E_f$ as a parameter. This "ferroelectric field" does not have the conventional meaning of the internal electric field as calculated by Känzig[5] but describes as an additional ligand field the change of the chemical bonding at the phase transition. As the wave functions are not exactly known, only an estimate of the half-life change is given and no exact calculation is attempted.

2. *The ferroelectric field.* Känzig[5] calculated for the point dipole and for the pure ionic crystal model the internal electric fields at the site of the different ions in the ferroelectric BaTiO$_3$. The values for the Ti ion are compiled in table I.

In the paraelectric phase of BaTiO$_3$ the internal electric fields are not zero, but are no longer intramolecularly coupled. The order of magnitude of the internal electric fields of BaTiO$_3$ in the paraelectric and ferroelectric phases is essentially the

TABLE I

| Internal electric field at the site of the Ti ion as a function of the crystal model[5] | |
| --- | --- |
| Ionic crystal model | $0.59 \times 10^8$ V/cm |
| Point dipole model | $2.64 \times 10^8$ V/cm |

same. The difference in detail of both fields gives us the additional ligand field, which is in this case the "ferroelectric field".

For a spontaneous polarization of $16\ \mu C/cm^2$ at the para-ferroelectric phase transition ($T_c = 120\,°C$) a change of ca. 23 Å in the optical absorption band edge at about 4000 Å was observed[6]. Interpreted by the ligand-field theory[7] this indicates a relative change of the ligand-field parameter 10 Dq by $5.8 \times 10^{-3}$. To find a rough numerical value for the "ferroelectric field" one can calculate the absolute change of the internal electric field from table I by the relative change in the ligand-field parameter, assuming a proportionality[7] between the internal electric field and 10 Dq. The results are presented in table II.

TABLE II

| The "ferroelectric field" at the site of the Ti ion in BaTiO$_3$ as a function of the crystal model | |
| --- | --- |
| Ionic crystal model | $0.34 \times 10^6$ V/cm |
| Point dipole model | $1.52 \times 10^6$ V/cm |

3. *Estimate of the half-life change.* It is well known that an electric field induces a change in the valence-electron density of an atom or ion. In the case of an ion which is at a site of the crystal lattice with no inversion symmetry, the change of the valence-electron density is directly proportional to the electric field strength[4]. For the ferroelectric phase of the BaTiO$_3$ crystal this symmetry condition is fulfilled for the Ti(Zr) site. For a first approximation of the change in the electron density $\Delta\ |\psi(0)|^2/|\psi(0)|^2$ of $^{89}$Zr one can equate it with the change of the valence-electron density. For a more precise estimate or a calculation one should consider in addition Sternheimer shielding or antishielding effects and use exact wave functions for the Zr ion.

According to Bloembergen and Dixon the following relation between the change of the valence-electron density and an electric field can be obtained[4]:

$$\left| \frac{|\psi(E_f)|^2 - |\psi(E_f = 0)|^2}{|\psi(E_f = 0)|^2} \right| \approx \frac{eR}{\sqrt{2}\,\Delta}\ |E_f|,$$

where $R$ is the interatomic distance Ti–O, $\varDelta$ is the energy difference between the binding and antibinding molecular orbital and $E_f$ is the electric field strength. For the actual estimate of $\varDelta\lambda/\lambda \approx \varDelta \ |\psi(0)|^2/|\psi(0)|^2$ the following numerical values were used: R $\approx$ 1.9 Å (mean distance Ti–O at room temperature[6])), $\varDelta = 3.1$ eV (activation energy calculated from the absorption band edge at 4000 Å).

The numerical result of this estimate is presented in table III as a function of the crystal model together with the experimental result.

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TABLE III

Theoretical estimate and experimental result for the change of the decay constant $|\varDelta\lambda/\lambda|$ of $^{89}$Zr in BaTi(Zr)O$_3$

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| | $|\varDelta\lambda/\lambda|_{est.}$ | $|\varDelta\lambda/\lambda|_{exp.}$ |
|---|---|---|
| Ionic crystal model | $1.47 \times 10^{-3}$ | $(0.80 \pm 0.03) \times 10^{-3}$ |
| Point dipole model | $6.51 \times 10^{-3}$ | $(0.80 \pm 0.03) \times 10^{-3}$ |

So far only the absolute value of the estimated half-life change was considered. The experimental result shows a decrease of the decay constant of $^{89}$Zr in the ferroelectric BaTi(Zr)O$_3$[2]). This means that the Ti ion carries in the ferroelectric phase a higher positive charge than in the paraelectric phase of BaTiO$_3$. Interpreted by the ligand-field theory this gives a higher ligand field, which is consistent with the shift of the optical absorption band edge at about 4000 Å towards higher energies, when the para-ferroelectric phase transition of BaTiO$_3$ occurs[6]).

4. *Discussion*. As is shown in table III the theoretical estimates and the experimental result show essentially the same order of magnitude. It must be emphasized that the paper does not give exact values but the idea was to depict a rough model for a possible explanation of the measured half-life change of $^{89}$Zr in BaTi(Zr)O$_3$. The estimated values of $\varDelta\lambda/\lambda$ (table III) are higher than the experimentally determined values, but this is not surprising, as no screening potential, overlap integrals of the wave functions and Sternheimer shielding (antishielding) effects were taken into account. For an exact calculation suitable molecular wave functions should be used which in addition make a difference between the different types of oxygen ions in the ferroelectric BaTiO$_3$.

As other experiments[8]) indicate, it is possible that only the change of the crystal structure at the phase transition is responsible for the change of the half-life and that the phenomenon of the "ferroelectricity" is of no importance. Yet, also under this assumption the estimate and the interpretation performed are valid, as the change of the crystal symmetry always affects the ligand fields.

## REFERENCES

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