Structural Phase Transitions in $BaTiO_3$ Studied via Perturbed Angular Correlations

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Phase transitions in the ferroelectric perovskite $BaTiO_3$ were studied for ^{111}In-implanted polycrystalline samples by measuring the electric field gradients by means of Perturbed Angular Correlation spectroscopy. The phase transitions between the orthorhombic ⇔ rhombohedral ⇔ tetragonal ⇔ cubic lattices were investigated in 2 - 10 K steps, for increasing and decreasing temperatures, in order to determine their hysteresis. The transition parameters are compared with results from measurements of the spontaneous polarization, electric susceptibility and neutron scattering.

Key words: Perturbed Angular Correlations; $BaTiO_3$; Phase Transitions; Hysteresis; ^{111}In.

1. Introduction

Among the perovskites, $BaTiO_3$ is the most important ferroelectric compound which is widely used in electromechanical actuators, sensors, ceramic capacitor dielectrics and photo-galvanic devices [1-3]. Its crystal structures, structural and electric phase transitions have been analyzed in much detail using several methods, such as neutron and X-ray diffraction, electric susceptibility, etc. Previous results from Perturbed Angular Correlation (PAC) spectroscopy in $BaTiO_3$, $Ba(TiHf)O_3$, and $CdTiO_3$ using ^{181}Hf/^{181}Ta probes have been reported by Catchen et al. [4 - 6] and by Schäfer et al. [7]. Recently, Uhrmacher and collaborators [8] have published first PAC results in $BaTiO_3$ using ^{111}In/^{111}Cd hyperfine probes. Their survey measurements showed the occurence of electric field gradients (EFG) in the non-cubic phases, present below the Curie temperature T_C = 393 K. Structural phase transitions can be monitored via PAC, if the hyperfine probe atoms substitute specific cation lattice sites. Several recent studies on perovskites of the type $A^{2+}B^{4+}O_3$ [9, 10] using ^{181}Hf and ^{111}In probe nuclei have given evidence that the main hyperfine fraction can be attributed to substitutional B-site implantation of the probes.

The present PAC measurements for ^{111}In/^{111}Cd probes in polycrystalline $BaTiO_3$ samples aim at scanning, in finer temperature steps than in [8], the structural phase transitions, which occur between the cubic phase (I, paraelectric), the tetragonal phase (II), the orthorhombic phase (III), and the rhombohedral phase (IV). The approximate transition temperatures are T_0 = 193 K for the IV ⇔ III transition, T_0' = 278 K for the III ⇔ II transition and T_C = 393 K for the II ⇔I transition [4 - 6, 8].

2. Experiments

The PAC measurements were carried out for polycrystalline $BaTiO_3$ powder samples of 99.995% purity which were pressed into pellets, 4 mm in diameter and 0.5 mm thick. Powder X-ray diffraction analyses at room temperature revealed that all observed reflexes could be assigned to the expected tetragonal phase. Some 10^{12} $^{111}In^+$ ions were implanted at 400 keV ion energy into the samples, using the Göttingen ion implanter IONAS [11]; the implantation depth was about 60 nm. After implantation the samples were annealed for four hours at 1673 K in air in order to remove radiation damage. For the measuring temperatures below 300 K, the samples were mounted at the pole tip of either a closed-cycle helium cryostate (T = 10 - 230 K) or a Peltier element (T = 275 - 296 K). Both cryostates were housed in vacuum chambers at pressures of 10^{-6} - 10^{-5} mbar. Measurements above room temperature

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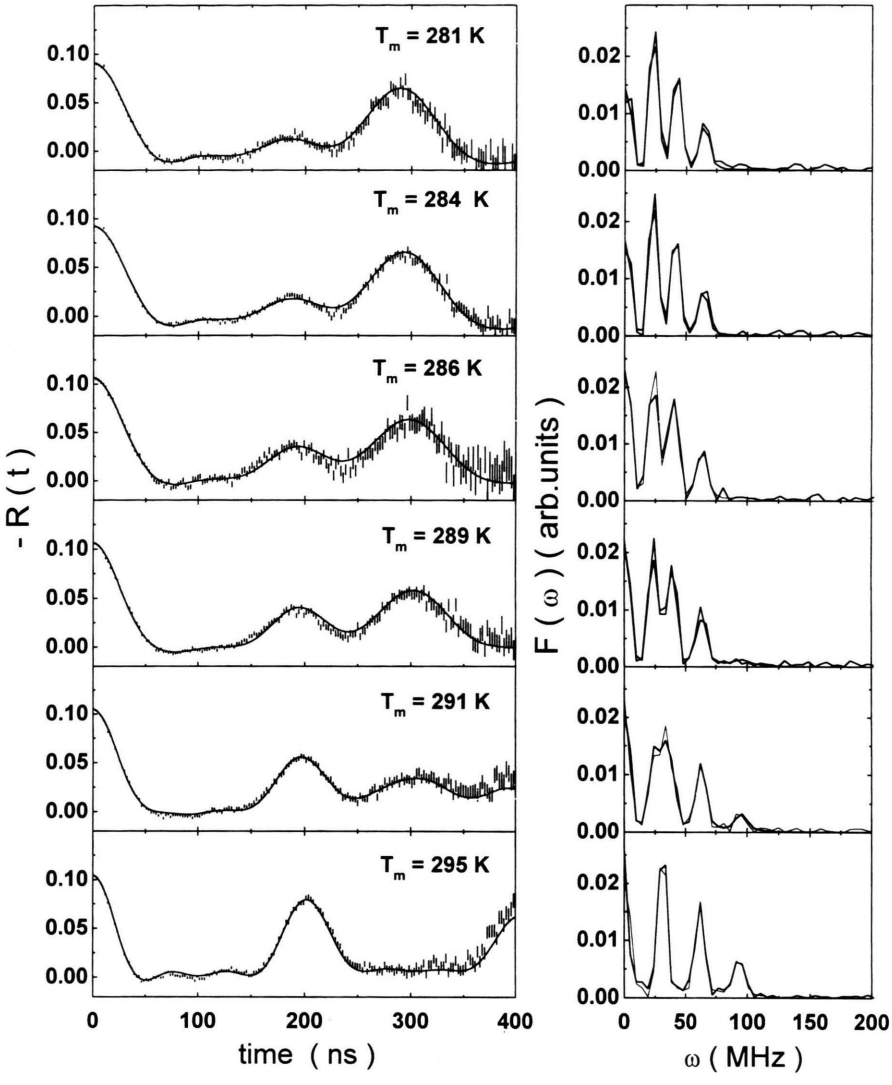

Fig. 1. Perturbation functions $R(t)$ and Fourier transforms $F(\omega)$ measured across the III → II phase transition.

were carried out under air in an oven of low γ-ray absorption. We estimate that the given temperatures are correct within better than ± 0.4 K.

The PAC spectra were accumulated using a set-up of four NaI(Tl) detectors in 90° geometry. The perturbation functions $R(t)$ were fitted by assuming, at each temperature, two fractions f_i and $f_k = 1 - f_i$, which are characterized by their respective *static* EFG parameters [12], i. e. the quadrupole frequency ν_Q, asymmetry parameter η and frequency width δ. Figure 1 illustrates the evolution of the perturbation function $R(t)$ and its Fourier transform $F(\omega)$ across the III ⇒ II phase transition, where the temperature was increased from 281 K to 295 K. Evidently, as shown in Fig. 2, the hysteresis of this phase transition shows up via the temperature dependences of the two competing fractions $f_{III}{}^{\uparrow/\downarrow}$ and $f_{II}{}^{\uparrow/\downarrow} = 1 - f_{III}{}^{\uparrow/\downarrow}$, for increasing or decreasing temperature. Finally, Fig. 3 displays the II ⇒ I phase transition which occurs very suddenly.

3. Electric Field Gradients and Site Occupation

The deduced EFG parameters for ^{111}Cd (and for ^{181}Ta [4 - 6]) measured in the various phases of $BaTiO_3$ are listed in Table 1. In the case of the ^{111}Cd probes, one notes symmetric EFG's in the phases II and IV ($\eta_{IV} = \eta_{II} = 0$), while the EFG of the phase

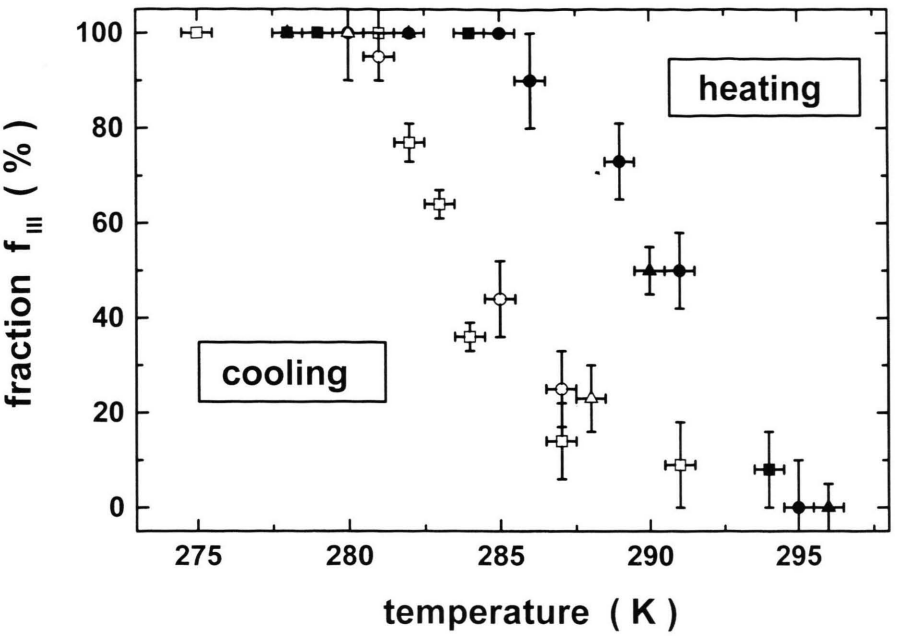

Fig. 2. Hysteresis of fraction III when heating (dots) or cooling (open squares) the sample across the III → II phase transition.

Table 1. Electric field gradients of ^{111}Cd and ^{181}Ta probes in $BaTiO_3$.

Phase	— ^{111}Cd —				— ^{181}Ta [4 - 6] —			
	T (K)	ν_Q (MHz)	η	δ (MHz)	T (K)	ν_Q (MHz)	η	
IV, rhomboh.	80	6.3(24)	0	3.1(16)	80	63(17)	0	
III, orthorh.	227	22.0(8)	0.37(6)	1.1(6)	220	137(12)	0.4(1)	
II, tetrag.	293	33.3(7)	0	1.4(5)	293	205(12)	0	
I, cubic	475	0	0	43(10)	400	0	0	

III is asymmetric, η_{III} = 0.37(6). All EFG's are well defined, with the width parameters being only δ = 1 - 3 MHz. When comparing the EFG parameters for ^{111}Cd and ^{181}Ta probes, we note that the asymmetry parameters η agree fairly well for the various phases. Furthermore, the ratios of the quadrupole frequencies ν_Q for both probes agree with the ratio $\nu_Q(^{181}\text{Ta})/\nu_Q(^{111}\text{Cd})$ = 6.5(10) predicted by the point charge model for the B-site, if we infer the appropriate quadrupole moments and Sternheimer factors of the two probe nuclei. This agreement of asymmetry parameters and frequency ratios thus strongly supports that both types of probe ions are being implanted into the B-site and substitute Ti. This conclusion is supported by PAC measurements with ^{181}Hf/^{181}Ta probes in $SrHfO_3$ and $BaHfO_3$ perovskites, following

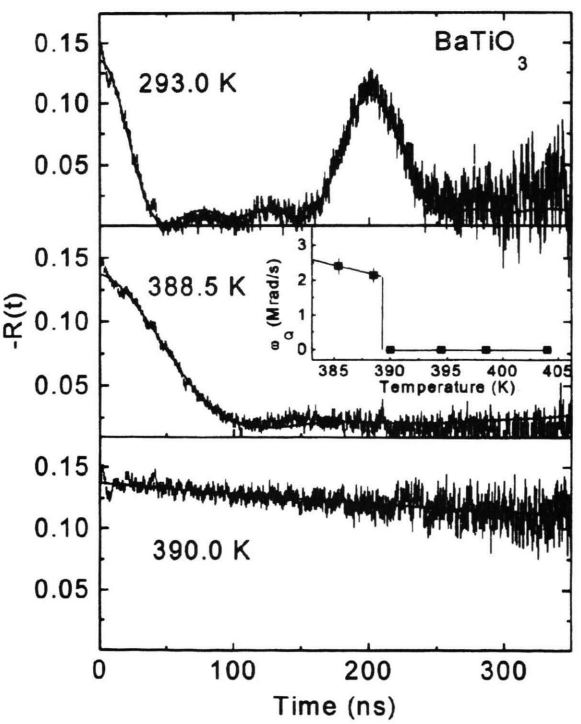

Fig. 3. Perturbation functions for ^{111}Cd in $BaTiO_3$ as observed near the II → I phase transition. The inset shows the temperature dependence of the quadrupole frequency ω.

neutron activation of ^{180}Hf [9], and in our previous paper on ^{111}In/^{111}Cd in $BaTiO_3$ [8]. Similar results have also been discussed by Luthin et al. [13] for ^{111}Cd in ZrO_2 and HfO_2 and by Wiarda et al. [14] for a large number of other binary oxides.

4. Phase Transition Parameters

Let us now discuss, for the three phase transitions in $BaTiO_3$ considered, the temperature dependence of the fractions $f^{\uparrow/\downarrow}$ that reveal the hysteresis. As usual, we introduce the transition temperatures $T_0^{\uparrow}$ and $T_0^{\downarrow}$, at which the two competing fractions are equal when increasing or decreasing the temperature across a phase transition. The quantity $\delta T_0 \equiv |T_0^{\uparrow} - T_0^{\downarrow}|$ measures the width of the hysteresis. The "smoothness" of a phase transition can be expressed by the quantities $\Delta T^{\uparrow}$ and $\Delta T^{\downarrow}$, where we used the approximation

$$f^{\uparrow/\downarrow}(T) = \{1 \pm \exp[(T - T_0^{\uparrow/\downarrow}/\Delta T^{\uparrow/\downarrow}]\}^{-1}$$

for that fraction which has disappeared well *above* the transition temperature $T_0^{\uparrow/\downarrow}$. In Table 2, the deduced transition parameters are compared with the values reported from neutron diffraction, electric susceptibility and polarization experiments [1, 15, 16]. Only in the case of the III → II transitions have we been able to obtain precise values of $T_0^{\uparrow/\downarrow}$ and $\Delta T^{\uparrow/\downarrow}$ = 1.7(2) K.

We first notice that the widths parameter δT_0 generally decreases for increasing transition temperatures, i. e. $\delta T_0^{IV\to III} \approx 7.5$ - 25 K, $\delta T_0^{III\to II} = 6$ K, and $\delta T_0^{II\to I} < 2$ K. Furthermore, the transition temperatures $T_0^{\uparrow/\downarrow}$ themselves measured with different methods do not agree with each other. A possible explanation has been given by Zhong et al. [17] who found that the annealing conditions of the samples determine the grain size and consequently the transition parameters. In this way, changes of $T_0^{\uparrow/\downarrow}$ by as much as 10 K have been observed, if the annealing temperature varies between 1273 K and 1423 K.

Table 2. Transition parameters in $BaTiO_3$ as obtained with different methods.

Transition	$T_0^{\uparrow}$ (K)	$T_0^{\downarrow}$ (K)	δT_0 (K)	Method	Ref.
IV→III	202.5	195	7.5	PAC, ^{111}Cd	Present work
	203	178	25	Polarization	
	195	178	17	Susceptibiliy	[15]
III→II*	290.4(2)	284.3(3)	6.1(3)	PAC, ^{111}Cd	Present work
	274	269	5	PAC, ^{181}Ta	[7]
	284	278	6	Neutron diffr.	[16]
	276	270	6	Polarization	
	277	270	7	Susceptibilty	[15]
II→I		389	< 2	PAC, ^{111}Cd	Present work

* $\Delta T^{\uparrow}$ = 1.6(2) K; $\Delta T^{\downarrow}$ = 1.8(3) K.

In conclusion, we have determined the electric field gradients of dilute ^{111}Cd impurities in polycrystalline $BaTiO_3$ samples. For each of the known phase transitions, we have deduced the EFG parameters, the transition temperatures $T_0^{\uparrow/\downarrow}$ and, in the case of the orthorhombic ⇔ tetragonal (III ⇔ II) transition, the average smoothness parameter $\Delta T^{\uparrow/\downarrow}$ = 1.7(2) K. In view of the different values of $T_0^{\uparrow/\downarrow}$ observed with various methods, PAC measurements in single-crystals are required in future experiments. Furthermore, the influence of an external electric field on the EFG parameters also appears to be an interesting extension of the present study.

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