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Ferroelectric phase transition in barium titanate nanoparticles

P. Sedykh[1,2] and D. Michel[1,*]
[1]*Faculty of Physics and Geosciences, University of Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany*
[2]*Faculty of Physics, St. Petersburg State University, Ulyanovskaya street 1, 198504 St. Petersburg, Russian Federation*

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Size-dependent changes were found in the ^{137}Ba NMR spectra of ensembles of very small $BaTiO_3$ particles. The NMR line shapes were studied at different Larmor frequencies over a broad temperature range. In the tetragonal phase, the NMR lines may be decomposed into a contribution typical for the line shape of bulk samples ("ordered" part) and a part in which the tetragonal symmetry is no longer visible ("disordered" part). Both contributions reveal typical changes when the temperature is varied in the range of the tetragonal phase, i.e., between approximately 400 and 300 K. The "ordered" part reveals a first-order phase transition at temperature T_f which decreases when the particle size becomes smaller. As is known, in the case of bulk material the quadrupole coupling constant C_Q may be related to the order parameter (spontaneous polarization P_S). Therefore, for all samples the temperature dependence of the C_Q in the "ordered" part was studied in the whole tetragonal phase. Its temperature dependence below T_f, with a jump at the first-order phase transition, can be described by an exponential law $C_Q \propto (T_f - T)^{\beta}+\text{const}$ for $T < T_f$, in analogy to the Landau theory, but the parameter β is less than $\frac{1}{2}$. The "disordered" part shows no jump at T_f where its quadrupole coupling constant is approximately zero. The data are used to discuss a structural model for the fine particles.

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I. INTRODUCTION

Barium titanate-based dielectrics are especially interesting because of their high permittivity values. They play a great role in applications. In this context, it is very interesting to know how the material properties of barium titanate change if the particle size is reduced. In our recent paper,[1] ^{137}Ba NMR studies were performed on samples of small particles of $BaTiO_3$ and it was shown that these are very sensitive to changes in the structure of the particles. In this work, the same samples were used as investigated in previous NMR and EPR studies.[1–3] The measurements were carried out on samples of nanoparticles of $BaTiO_3$ with grain diameters between 15 and 155 nm. The results are compared to polycrystalline material of $BaTiO_3$ ("bulk"). The average diameter of particles for the polycrystalline sample was larger than about 500 μm. To monitor the influence of the grain size on the properties of fine powders, the temperature dependence of the ^{137}Ba NMR line shape will be studied. A temperature range will be considered which covers the paraelectric (cubic)-ferroelectric (tetragonal) phase transition and the tetragonal phase for bulk barium titanate.

The phase transitions in $BaTiO_3$ are known to be of the displacive type.[4–6] The transverse-optical soft mode which is indicative of displacive behavior, however, is overdamped near the phase transition around 403 K.[7–10] A possible coexistence of displacive (underdamped soft mode) and order-disorder components (strongly overdamped or relaxor dynamics) in the mechanism of the phase transition has been discussed.[11–15] This complex behavior may explain why there is still a debate about the character of the phase transition.[14–18] By means of EPR measurements on Fe^{3+} sites, Müller and Berlinger[14] probed the local potential. The results point to a strong local Ti anharmonicity in $BaTiO_3$ as compared to the motion of Ti ions in a much more harmonic potential in $SrTiO_3$, where soft-underdamped ferroelectric modes dominate. Although the debate concerning the nature of the phase transition still continues, this special question will not influence the interpretation of our data. Recently, by means of ^{47}Ti and ^{49}Ti NMR, the presence of off-center Ti sites has been observed even in the cubic phase of a very pure $BaTiO_3$ single crystal.[19] Previous Ba and Ti NMR studies on $BaTiO_3$ samples[20–23] have revealed no cubic symmetry breaking and no satellite transitions in the NMR spectra above the cubic-tetragonal phase transition. The Ba quadrupole coupling constant C_Q was found to be proportional to P_S^2.[20,23] The Ba quadrupole coupling tensors were determined in the tetragonal, orthorhombic, and rhombohedral phases of multidomain $BaTiO_3$ crystal.[24] Furthermore, the estimation of the principal values of the quadrupole tensors has been controlled by means of measurements on polycrystalline $BaTiO_3$ samples obtained from the same crystals. The conclusions drawn from measurements on single crystals are in a very good agreement with the results of the ^{137}Ba NMR line-shape measurements on powdered samples. This rather clear situation has encouraged us to apply ^{137}Ba NMR spectroscopy also to the more complex situation that occurs for fine particles. The investigations are based on a detailed analysis of the ^{137}Ba NMR line shape as presented in our previous paper.[1] Here we show that a decomposition of the lines into two contributions may occur and this may be related to the structure of the fine particles. In the tetragonal phase, the NMR lines may decompose into a component typical for the line shape in that phase (denoted here as the "ordered" part) and a part in which the tetragonal symmetry is no more noticeable (denoted as the "disordered" part). In order to investigate the effect of the particle size on properties of the fine particles' NMR line shape, an extensive study of temperature dependence of the ^{137}Ba NMR spectra is undertaken in the present study. Measurements were run in the cubic and tetragonal phases of $BaTiO_3$. They are particularly interesting because the quadrupole coupling constant, which

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can be measured in the tetragonal phase, is directly related to the ferroelectric order parameter (i.e., the spontaneous ferroelectric polarization). We compare the data measured for samples of small particles with results derived for the $BaTiO_3$ bulk material. In this case, a comparison with the Landau theory for phase transitions is possible. This allows us to derive conclusions about ferroelectricity in our fine particles.

II. EXPERIMENTAL

The NMR spectra were measured at Larmor frequencies of 44.466 MHz ($B_0=9.4$ T), 55.578 MHz ($B_0=11.7$ T), and 83.361 MHz ($B_0=17.6$ T), using Bruker NMR spectrometers. We applied a two pulse echo sequence with a 16 step phase cycle where the whole echo decay was acquired and Fourier transformed to give the absorption line shape. The temperature range of the measurements was 420–296 K. ^{207}Pb NMR measurements on $Pb(NO_3)_2$ samples were made for the temperature calibration. Thus, an accuracy in the temperature measurements was achieved which was better than 0.5 K. High-field NMR measurements using the AVANCE 750 Bruker spectrometer (83.361 MHz) were run only at room temperature. $BaCl_2$ aqueous solutions were used as reference samples for ^{137}Ba NMR.

The microcrystalline material was prepared from a $BaTiO_3$ single crystal. This (multidomain) single crystal was grown by Albers[15,23] from the University of Saarland. The particle size distribution of the polycrystalline powder sample was analyzed by means of a light microscope. A mean grain-size diameter of about 500 μm (root-mean-square error 15 μm) was estimated. The particle size distribution in this case is well described by the Gaussian function.

Fine powders were prepared from a monomeric metallo-organic precursor through combined solid-state polymerization and pyrolysis.[2,25] This particular preparation route enables an adjustment of the mean particle size over a wide range from a few nanometers up to micrometer size. The resulting particle size is determined by the reaction atmosphere and the reaction temperature. The size dependence on the tempering temperature was carefully controlled by means of x-ray diffraction (XRD).[2,25] The product (yield 97%) was verified with the aid of elemental analysis and various spectroscopic methods, such as FT Raman, as well as by recording the x-ray absorption near-edge structure (XANES) at the Ti K edge.[26]

III. RESULTS

A. Measurements on polycrystalline $BaTiO_3$

In the ^{137}Ba NMR measurements on $BaTiO_3$ powders, only the central line transition ($m=+\frac{1}{2}\Leftrightarrow m=-\frac{1}{2}$, spin quantum number $I=3/2$ for ^{137}Ba nuclei) was studied (Fig. 1). Within the temperature range between approximately 404 and 296 K of the tetragonal phase, which is mainly studied here, the line shape shows the edge singularities characteristic for the axial symmetry of the quadrupole tensor where the asymmetry parameter η_Q of the quadrupole tensor is zero. In this phase, the ^{137}Ba NMR spectra were measured at three different dc magnetic fields ($B_0=9.4$, 11.7, and 17.6 T). The proportionality of the distances between the edge singularities to $1/B_0$ was observed[1] as expected if the second-order perturbation theory of the quadrupole interactions is applied. Hence it may be concluded that the line shape is dominated by the quadrupole coupling tensor. Hence, for the polycrystalline bulk material of $BaTiO_3$, the quadrupole coupling constant $C_Q=|e^2qQ/h|$ in the tetragonal phase can be directly derived from the distances of the edge singularities.[1] Our measurements of C_Q of microcrystalline barium titanate are in a very good agreement with those performed on single crystals of $BaTiO_3$ (Refs. 20 and 22–24) and polycrystalline material.[21,24] Relatively sharp ^{137}Ba NMR lines, with a Gaussian line shape and widths at half heights of about 150 Hz, were observed for the polycrystalline material in the cubic phase above the Curie temperature T_C where the electric field gradient is zero (an example of the NMR line shape of a $BaTiO_3$ polycrystalline sample at high temperature is presented in Ref. 21, for instance). Since the Curie temperature T_C for a first-order phase transition lies between the stability limits of the ferroelectric (T_f) and the paraelectric phase (T_p), we use only T_f in the following [see Eq. (1)]. The NMR lines are broadened abruptly at the phase transition from the cubic into the tetragonal phase (Fig. 2). It is known[20,23] that the square η^2 of the order parameter $\eta=P_S(T)/P_S(0)$ is proportional to the quadrupole coupling constant $C_Q\propto\eta^2$. The order parameter η near the cubic-tetragonal phase transition of $BaTiO_3$ can be satisfactorily described by the following equation obtained from the usual Landau expansion of the free-energy density f for a first-order transition:

$$\left(\eta^2+\frac{B}{2C}\right)^2=\frac{A}{C}(T_f-T). \qquad (1)$$

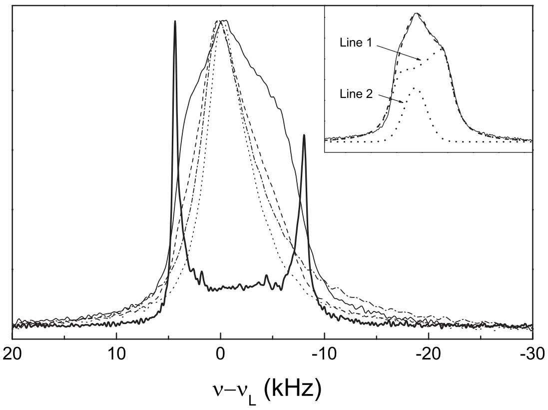

FIG. 1. Experimental ^{137}Ba NMR spectra of polycrystalline $BaTiO_3$ and powder samples of fine $BaTiO_3$ particles. Bold solid line: bulk sample; solid line: mean particle diameter of 155 nm, dashed line −75 nm, dotted line −25 nm, and dashed-dotted line −15 nm. The measurements were run at a dc magnetic field of 17.6 T at room temperature. An example of the NMR line-shape analysis is shown in the inset. Here the solid line illustrates the experimental spectrum and the dashed line the simulated spectrum. Lines 1 and 2 visualize the “ordered” part and the “disordered“ part of the fine particles, respectively.

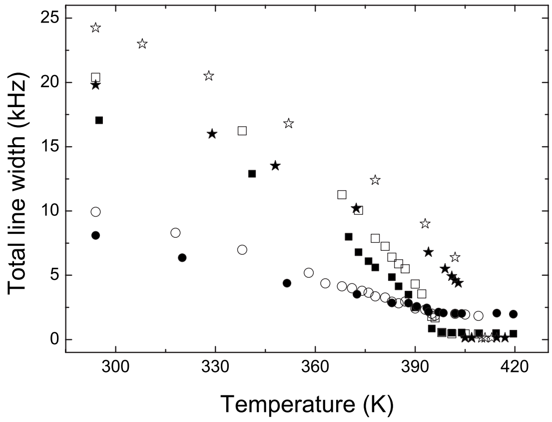

FIG. 2. ^{137}Ba NMR line width vs temperature for polycrystalline sample (stars) and for samples with mean particle diameters of 155 nm (squares) and 15 nm (circles) at dc fields of 9.4 T (open symbols) and 11.7 T (close symbols).

Here the constants are $A>0$, $B<0$, and $C>0$, $T_f=T_p+B^2/4AC$ is the upper stability limit of the ferroelectric phase and T_p characterizes the lower stability limit of the paraelectric phase. Our ^{137}Ba NMR line-shape measurements for the microcrystalline barium titanate have again confirmed that the experimental values of C_Q linearly depend on the quantity $(T_f\text{-}T)^{1/2}$ as expected from the Landau theory,

$$\eta^2 = \left[\frac{A}{C}(T_f - T)\right]^{1/2} - \frac{B}{2C} \propto C_Q \propto (T_f - T)^{1/2} + \text{const.} \tag{2}$$

In this relationship, a value $T_f=403.5$ K is chosen. Our measurements on the microcrystalline material have shown that the respective particle size (500 μm) is still large enough that size effects do not influence the cubic-tetragonal phase transition in a measurable way.

B. Measurements on fine particles

The influence of BaTiO$_3$ particle size on the central transition ^{137}Ba NMR spectra is clearly reflected in the measurements carried out in the temperature range [between 296 K (see Fig. 1) and approximately 420 K] of the tetragonal phase and above the phase transition into the cubic phase. As is mentioned above, for the polycrystalline sample ("bulk" sample), the cubic to tetragonal phase transition was characterized by an abrupt change in the line width (and correspondingly in C_Q), as expected for a first-order transition. Relatively narrow NMR lines were measured for this sample in the cubic phase and their line width (e.g., full width at the half height of the NMR line) did not depend on the dc magnetic field strength. This finding is in agreement with the (simple) fact that the electric field gradient and the spontaneous polarization are zero in the cubic phase. For the small particles (with mean diameters between 155 and 15 nm), a similar behavior was observed in the tetragonal phase (Fig. 2). The line width increases toward lower temperatures, but the abrupt change at the tetragonal-cubic phase transition is more and more smeared when the size of particles is reduced. Moreover, at temperatures below the phase transition, the line widths become smaller if the B_0 field is enhanced. If measurements are run at the magnetic fields of 9.4 and 11.7 T, the line width changes by a ratio of 1.25 ± 0.05 well reflecting to the proportionality to $1/B_0$. This experimental fact indicates the dominance of quadrupole interaction in this temperature range, as it was also found for the polycrystalline sample.

Above the (ferroelectric) phase transition, we can see that the total line width no longer depends on the temperature and an additional line broadening is seen for small particles (Fig. 2). For all samples with small particle sizes, the line width is larger in the temperature range of the cubic phase than that of the polycrystalline (bulk) material. Hence, it is probable that the additional broadening is due to a particle size-dependent distribution of chemical shifts. In the temperature range of the cubic phase, the line broadening for the samples with mean diameters of 25 and 15 nm is slightly enlarged if the external dc field B_0 is increased (Fig. 2). For larger particle sizes (155 and 75 nm) there is practically no change if B_0 is increased. It means that in the case of 25 and 15 nm particle samples, the situation is completely opposite to that in the tetragonal phase, where the line width is larger for a smaller magnetic field. This fact supports the above suggestion concerning an influence of the particle size distribution on a line width in the cubic phase. The behavior also indicates that there is no broadening due to the quadrupole interaction above the phase transition. We should mention here that since the increase in the line width with rising B_0 is only detectable for the smallest particles and since the linear increase in line widths (expected in case of chemical shift anisotropy) cannot be inferred from these data, a further discussion of the field dependence of the line shape for the smallest particles at higher temperatures will not be carried out here.

Because at higher temperatures the line broadening in the NMR spectra for small particles sizes is temperature independent and shows another broadening mechanism, it seems reasonable to subtract this constant line width in the further discussion of the data in the total temperature range considered. Please note that this small data adjustment is only essential close to the phase transition and does not play any role in the interpretation of the experimental data for temperatures of 5 K more and below T_f because, as mentioned, the broadening increases considerably at lower temperatures due to the quadrupole coupling.

As already mentioned above, the line shape in the tetragonal phase can be explained by a superposition of two contributions (see the inset in Fig. 1). The first one denoted as the "ordered" part reveals the line shape typical for the bulk sample in the tetragonal phase (line 1 in Fig. 1). For the second contribution, a Gauss-Lorentzian shape is observed and the typical features of the tetragonal symmetry are no longer noticeable (line 2 in Fig. 1). This part is referred to as the "disordered" part in the following discussion. Details of the numerical line-shape analysis are treated in our previous paper[1] and are therefore not described here.

For all samples, the temperature dependence of the quadrupole coupling constant C_Q for the "ordered" part in the small particles was studied in the temperature range between

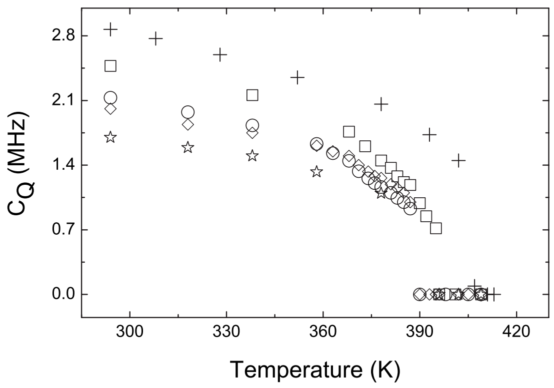

FIG. 3. Temperature dependence of the quadrupole coupling constant C_Q for the "ordered" part of samples of fine BaTiO$_3$ particles. For comparison, C_Q values for microcrystalline barium titanate sample are plotted (cross symbols). Squares −155 nm sample, circles −75 nm sample, stars −25 nm sample, and diamonds −15 nm sample.

approximately 400 and 300 K. The "ordered" part indicates a first-order-like phase transition at the temperature T_f where a jump in the quadrupole coupling constant C_Q is seen for all particle sizes and where C_Q is zero in the cubic phase (Fig. 3). Preliminarily we may estimate from the jump that the phase-transition temperature T_f is reduced when the particle size becomes smaller. Below the phase-transition temperature $T<T_f$, the temperature dependence of C_Q for the fine particles may be described by an exponential law,

$$C_Q \propto \eta^2 \propto (T_f\text{-}T)^\beta + \text{const}, \tag{3}$$

similarly as derived from Eqs. (1) and (2) but the parameter β is less than $\frac{1}{2}$ that predicted by the Landau theory for the bulk sample. Examples for this analysis are given in Fig. 4.

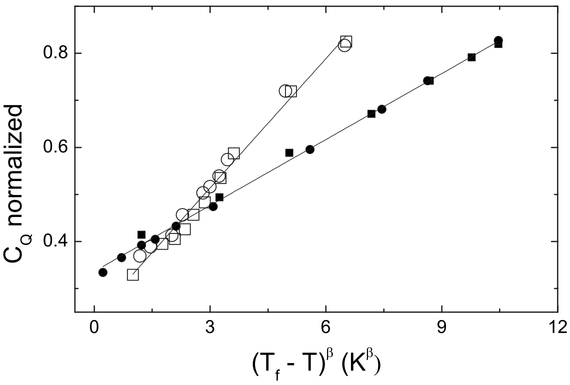

FIG. 4. C_Q versus $(T_f\text{-}T)^\beta$ for the polycrystalline BaTiO$_3$ sample (close symbols) and the 155 nm particle sample (open symbols). Please note here that we have omitted the constant part for the polycrystalline sample [see Eq. (2)], in order to enable a better comparison with the plot for the small particles. The experiments were run at two dc magnetic fields B_0=9.4 T: squares and B_0=11.7 T: circles. The data obtained for C_Q are independent of B_0 as expected (see text). Using all data points presented here, the line shown is the result of a linear regression leading to the values β=0.41 and T_f=391 K for the case of fine powders. For the polycrystalline material, we have found β=0.5 and T_f=403.5 K.

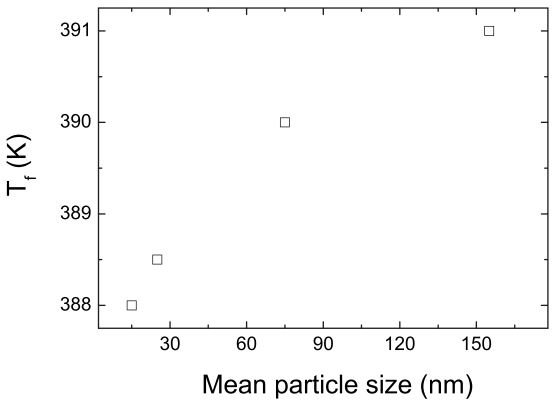

FIG. 5. Phase-transition temperatures T_f for various particle sizes.

The constant value in Eq. (3), which is zero above T_f, reflects the typical jumplike behavior at the first-order phase transition. In Fig. 4 we also plot the experimental data for the bulk sample according to Eq. (2) (for a better comparison, we have omitted here the constant part). The empirical plot of the measured quadrupole coupling constant C_Q for the small particles versus the quantity $(T_f\text{-}T)^\beta$ not only allows an estimation of the parameters β but also the derivation of the temperatures T_f (Fig. 5). The values T_f determined in this way approximately agree with the phase-transition temperatures estimated from the jump in C_Q. This agreement may also be a hint that the empirical description of the temperature dependence of the experimentally obtained quadrupole coupling constants C_Q by a power law leads to a consistent picture and is physically meaningful.

The "disordered" part in the small particles also reveals a continuously increasing line width when the temperature is lowered below the phase-transition temperature (Fig. 6). Close to the temperature T_f, the line width of the "disordered" part continuously merges into the constant value measured in the cubic phase. The latter constant part can be subtracted because it is not related to the behavior in the tetragonal phase (see the discussion above). Thus, we find that the behavior of the "disordered" part is similar to that

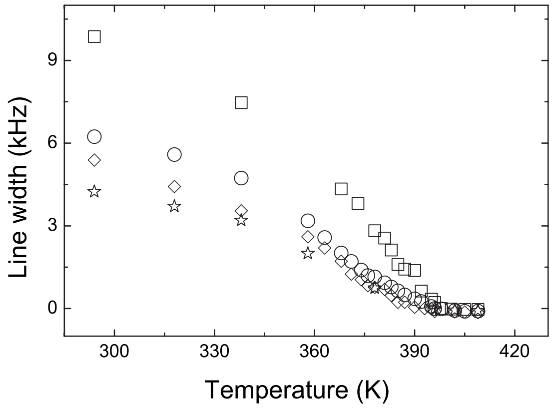

FIG. 6. Temperature dependence of the line width of the "disordered" part of samples of fine BaTiO$_3$ particles. Squares −155 nm sample, circles −75 nm sample, stars −25 nm sample, and diamonds −15 nm sample.

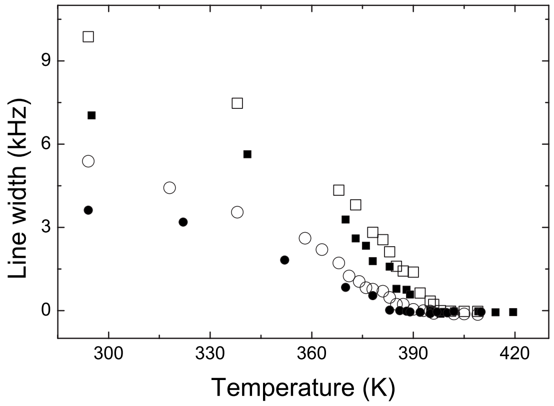

FIG. 7. Temperature dependence of the line width of the “disordered” part for 155 nm (squares) and 15 nm (circles) particle samples of $BaTiO_3$ shown for two different dc fields B_0=9.4 T (open symbols) and 11.7 T (close symbols).

expected for a second-order phase transition. For the further discussion, it is interesting to prove again whether the quadrupole coupling is also responsible for the line broadening of the “disordered” part in the temperature range where the “ordered” part reflects the tetragonal symmetry. Therefore, field-dependent measurements were carried out for the four nanosized samples. In the whole temperature range as mentioned, a proportionality of the line width to $1/B_0$ is also found for the “disordered” part (Fig. 7). Experimental ratio between the line widths observed at the magnetic fields of 11.7 and 9.4 T was again 1.25 ± 0.05 for measurements on samples with different particle sizes. Accordingly, there is no doubt that the line broadening below T_f is dominated by the quadrupole coupling in this case. Hence, from the line width of the “disordered” fraction of the fine particles, a mean quadrupole coupling constant $C_{Q,\mathrm{dis}}$ may be estimated. It is quite obvious that there is a continuous increase of $C_{Q,\mathrm{dis}}$ with lowering temperature $T_f - T > 0$. Since the quadrupole coupling constant in the case of the bulk specimen and the “ordered” fraction is directly related to the square of the spontaneous polarization, the behavior of $C_{Q,\mathrm{dis}}$ also points to a relationship between $C_{Q,\mathrm{dis}}$ and the electric polarization in the case of the “disordered” part. The Gauss-Lorentzian line shape for this part no longer shows, however, a relation to the tetragonal symmetry. Hence, $C_{Q,\mathrm{dis}}$ seems not to be directly related to the tetragonality parameter $\frac{c}{a}-1$ or to the square of the spontaneous polarization as found for the “ordered” fraction and also for the bulk sample.

Figures 8 and 9 show the temperature dependence of the relative fractions of the two contributions discussed above. One can see that in the case of both the 155 and 75 nm particle samples, the component fractions do not noticeably change below the phase transition, while the fraction of the “ordered” part is larger in the 155 nm particle sample than that in the sample with the smaller grain size. This means that the fraction of the “disordered” part is smaller in the 155 nm particle sample than in the 75 nm one. Please note that the accuracy for the estimation of these relative fractions in the vicinity of the phase transition from the tetragonal to the cubic phase is low. In particular, our method of NMR line deconvolution does not allow us to separate the influence of the quadrupole coupling and the size distribution of particles close to this transition by using the information from the relative fractions.

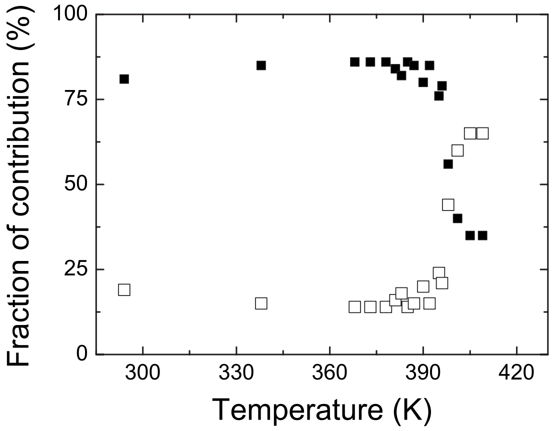

FIG. 8. Temperature dependence of the relative fractions of the two contributions for the 155 nm particle sample. The “ordered” part and the “disordered” part are denoted by close and open squares, respectively. Only the results of NMR measurements at a dc magnetic field of 11.7 T are shown because they are independent of the magnetic field applied.

IV. DISCUSSION

The extensive temperature-dependent measurements performed here for the “ordered” and “disordered” parts point to a rather unhomogeneous structure of the fine particles. In comparison to the microcrystalline material, the temperature dependence of C_Q (related to the square η^2 of the order parameter) for the “ordered” part becomes less pronounced if the particle size decreases (see Fig. 3). As shown in Fig. 3, a first-order character of the phase transition for this part can be inferred for all samples. It is true that the linear relationship between the quadrupole coupling constant C_Q in the

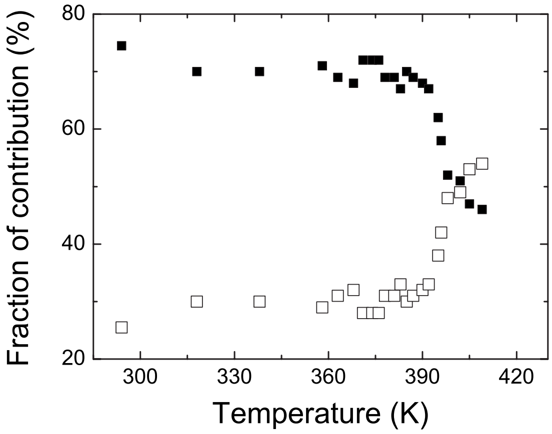

FIG. 9. Temperature dependence of the relative fractions of the two contributions for the 75 nm particle sample. The “ordered” part and the “disordered” part are denoted by close and open squares, respectively. Only the results of NMR measurements at a dc magnetic field of 11.7 T are shown (see also Fig. 8).

tetragonal phase and the difference $T-T_f$ to the phase-transition temperature can no longer be described by $(T_f\text{-}T)^{1/2}$ derived from the mean-field theory (T_f=403.5 K for the bulk sample). However, the experiments have shown that the coupling constant C_Q is proportional to $(T_f\text{-}T)^{\beta}$ +const. The exponent β as well as the phase-transition temperature T_f depends on the particle size. The exponents change from 0.41 to about 0.33 if the size is varied between 155 and 15 nm. The temperatures T_f vary between 391 and 388 K. In these experiments, we could not reach the particle size limit where size-driven effects lead to a complete suppression of ferroelectricity. An important question is here in which way the values derived for T_f, β, and the quadrupole coupling constants C_Q are influenced by the distribution of particle sizes. For T_f and β, we have found a continuous decrease if we compare the values for four samples with the different mean particle sizes. But we observed only small differences between the samples of 25 and 15 nm mean particle diameter. The influence of the particle size cannot be excluded here because in both cases the distribution functions overlap. This phenomenon is more clearly reflected in the values derived for the constants C_Q. Here we observe that the constant C_Q for the particles with the mean size of 15 nm is even larger than for 25 nm. This finding is reflected in Fig. 3 when we consider the data, for instance, obtained at room temperature. The influence of particle size distribution, however, does not weaken the conclusions which we have drawn above.

Binder *et al.*[27–30] showed in numerous recent papers that analytical theories, such as those of the "mean-field" type, had difficulty in dealing with systems of fine particles. Monte Carlo simulations were applied very successfully. As far as the static critical behavior is concerned, it has been well established that anisotropic ferromagnets undergoing transition to the paramagnetic phase, fluids of molecules with short-range interactions, and other nanosystems, for instance, are affected due to external walls or surfaces or other boundaries and can be substantially modified in the bulk behavior. It has been shown that those systems belong to the universality class of the three-dimensional (3D) Ising model. Hence, a nontrivial description of finite-size effects with non-mean-field exponents is expected. Although a quantitative theoretical analysis of our present systems is still missing, we assume that the theoretical background known from the work of Binder *et al.* may help us to understand, at least qualitatively, our experimental situation. The exponents derived here for the nanoparticles have changed from the mean-field value $\frac{1}{2}$ for the bulk to values of about 0.3 which are close to the values derived for the order-parameter exponents on the basis of the 3D-Ising model. In a Monte Carlo study of an Ising ferromagnet on a simple-cubic lattice whose surfaces form a bipyramid, the authors found[27] that the spontaneous magnetization appears discontinuously in the limit where the dimension L diverges. They mention that one might indeed interpret this transition as a standard first-order transition, but actually it is rather a limiting case of the second-order phase transition. They point out that in a system that is finite in all its linear dimensions, no sharp transition occurs but rather the transition is rounded. Our data derived for the "ordered" part are not in contradiction with this conclusion, although above we have suggested a first-order character. Because the accuracy of our measurements for the small particles very close to T_f is not high enough, it seems to be problematic to differentiate between a clear first-order type and a "limiting" case of a second-order transition. Moreover, for the "disordered" part a continuous behavior close to T_f was clearly observed. In the light of this discussion, the conclusion of a second-order transition seems to be also convincing. Moreover, the line-shape analysis indicated strong local distortions which are beyond the limited tetragonal distortions normally occurring in the ferroelectric phase and which are reflected in the "ordered" part.

As we have already shown in more detail in our previous paper,[1] it is interesting to compare our ^{137}Ba NMR measurements on fine $BaTiO_3$ particles with EPR measurements on similar samples which contain Mn^{2+} ions as paramagnetic sites.[2] First of all, similar conclusions, which may be drawn from both the NMR and EPR measurements, reveal that the Mn^{2+} ions introduced as paramagnetic sites can be considered as isolated local probes which do not lead to a detectable change in the properties of the material. In the EPR spectra, the axial fine-structure term $DS_z^2-\frac{1}{3}S(S+1)D$ contains the major part of the structural information. In the approximation of the superposition model, the fine-structure parameter D is proportional to the square η^2 of the order parameter and, thus, contains the analogous information to the quadrupole coupling constant. The simulations of the EPR and NMR spectra are consistent with the following structural model for the fine particles. A weakly distorted tetragonal core is surrounded by a highly distorted shell where the local symmetry can only be characterized by a strong distortion of the internal electric fields. The fraction of the "disordered" regions increases when the particle diameters are reduced from 155 to 15 nm. For the sample with the smallest diameters (15 nm), the strongly "disordered" component dominates. Our picture of a small particle as an aggregate of inner regular core and heavily distorted outer layer mediated by the tetragonality gradient is consistent with that of Anliker *et al.*[31] and Niepce.[32] Anliker *et al.* derived a two-component model from their x-ray scattering and surface-sensitive electron-scattering experiments. Niepce discussed the so-called tetragonal anisotropy defect. The main qualitative conclusions may also be compared with those of Frey and Payne[33] and Tanaka and Makino.[34] Frey and Payne reported upper boundaries of $d\approx 40$ nm for regimes in which size effects might be manifest in barium titanate particles and a critical value of 9 nm. Tanaka and Makino supported an extrapolated value of $d\approx 10$ nm for the critical size at which the Curie temperature drops to zero. They explained that true size effects by an expansion of the lattice constant as the particle diameter d is reduced but not by the influence of depolarization fields. In an analytical approach, Glinchuk *et al.*[35,36] explained the properties of ferroelectric nanomaterial by the effect of the surface tension and depolarization field. In EPR studies on Cr^{3+} paramagnetic sites in $PbTiO_3$ particles, the mean particle diameter was varied between 210 and 6 nm. The normalized quantities of D, $\frac{c}{a}-1$, and the phase-transition temperatures T_f were extrapolated using the plot by Ishikawa *et al.*[37] and a critical diameter of approximately 6 nm for the size-driven ferroelectric phase transition in $PbTiO_3$ nanoparticles was estimated.[3]

V. CONCLUSION

^{137}Ba NMR measurements on $BaTiO_3$ samples of fine particles with mean diameters of 155, 75, 25, and 15 nm could be carried out in the tetragonal phase, near the phase transition to the cubic phase and at still higher temperatures. Only the central transition NMR spectra were measured. The experimental and calculated data were compared to those obtained for the microcrystalline barium titanate sample which could be taken as a reference for the "bulk" material. The data for the microcrystalline sample were in a good agreement with those taken from literature and obtained also in our previous work. For the analysis of the data, it is important that the spectra in the tetragonal phase are determined by the quadrupole coupling because it has been found for the bulk material that the quadrupole coupling constant can be directly related to the spontaneous ferroelectric polarization. Above the phase-transition temperature the spectra reflect the influence of the particle size and its distribution. A systematic line-shape analysis (deconvolution into two different parts) of the NMR spectra was carried out in the temperature range of the whole tetragonal phase. The so-called "ordered" part reveals still the tetragonal symmetry, whereas the second contribution can only be described by a Gauss-Lorentzian line shape and the typical features of the tetragonal symmetry are no longer noticeable here. Since the latter "disordered" contribution to the line shape is also determined by the quadrupole coupling, this part is consistent with the tetragonality gradient found in other work. The temperature dependence of the line shape of the "disordered" contribution shows a behavior at the phase transition which is similar to a second-order phase transition. In contrast, the quadrupole coupling constant for the "ordered" part (proportional to the spontaneous polarization) is a linear function of $(T_f\text{-}T)^{\beta}$ similarly as expected from the Landau theory of first-order phase transitions; but the parameter β and the phase-transition temperature depend on the particle size. Both effects are in accordance with theoretical predictions for size effects for ensembles of small particles.

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*FAX: +49 341 9732649; michel@physik.uni-leipzig.de

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