Perturbed Angular Correlation Studies in $SrTiO_3$ Single Crystals

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The quadrupole hyperfine interactions of ^{111}Cd/^{111}In probe nuclei in single-crystalline $SrTiO_3$ perovskite samples were investigated using Perturbed Angular Correlation spectroscopy. Three electric field gradients were detected and their fractions and hyperfine parameters were measured in the temperature range from 26 to 700 K. The fraction f_0 having a vanishing quadrupole frequency, as expected for ^{111}Cd on substitutional sites in a cubic lattice, starts to develop around 300 K and reaches 100% at 700 K. Two well-defined EFG's having closely lying quadrupole frequencies and asymmetry parameters of ω_{Q1} = 49.1(3) Mrad/s, η_1 = 0.10(2) and ω_{Q2} = 51.8(3) Mrad/s, η_2 = 0.12(2), at room temperature, were identified in the temperature range from 250 to 530 K, and their (100) orientation in the lattice was determined. They are associated with electronic defects at the probe atoms.

Key words: Perturbed Angular Correlations; $SrTiO_3$; Single Crystal; Electronic Defects; Perovskite.

1. Introduction

Investigations of the hyperfine interactions in ternary oxides using Perturbed Angular Correlation (PAC) spectroscopy with radioactive ^{111}In or ^{181}Hf nuclei have been carried out since several years [1 - 8]. Many of these investigations served to study the possible scaling of electric field gradients (EFG) with the cation-oxygen bond lengths [3, 5], the structural, magnetic or electric phase transitions [4, 6, 7], and the nature of electronic or ionic defects and their influence on the electric conductivity [9 - 11]. While in many compounds the probe atoms behave as ideal "observers" on substitutional cation sites, the ^{111}In tracers were found to have a strong influence on the phase transitions in the case of the antiferromagnetic ordering in $CuFeO_2$ [4] and the spin-Peierls transition of $CuGeO_3$ [6]. Previous PAC studies in a number of perovskite oxides revealed, besides substitutional probe sites, defect complexes which, however, are not understood up to now [2, 8 - 11].

In the present work, we extend our previous PAC experiments on ^{111}In/^{111}Cd probes in $BaTiO_3$, $BaHfO_3$ and $SrHfO_3$ perovskites [7,8] to $SrTiO_3$ single crystals, using implanted $^{111}In^+$ ions. On the basis of the cubic structure of the compound, one expects a vanishing EFG on substitutional, defect-free cation sites. Defective sites of non-cubic structure should therefore be easily identified on the basis of their EFG's.

2. Experiments

Single crystals of $SrTiO_3$, 1 cm^2 × 0.5 mm in size and with the surface oriented parallel to the $\{100\}$ or $\{111\}$ crystal planes, were implanted at room temperature with 280 keV $^{111}In^+$ tracer ions at a total fluence of about 10^{12} ions. The samples were annealed for 4 h in air at 1673 K to remove radiation damage. Rutherford backscattering spectroscopy in channeling geometry (using 0.9 MeV α-particles) and X-ray diffraction measurements did not show any differences between the virgin and ^{111}In-doped annealed samples. The PAC spectra were accumulated in two four-detector set-ups in 90° geometry, equipped with either NaI or BaF_2 scintillators. The sample surface was oriented along the intersecting line between the centers of two adjacent detectors so that the γ-rays were detected at 45° to the surface normal. Data were taken in a high-vacuum chamber at 26 - 300 K or in

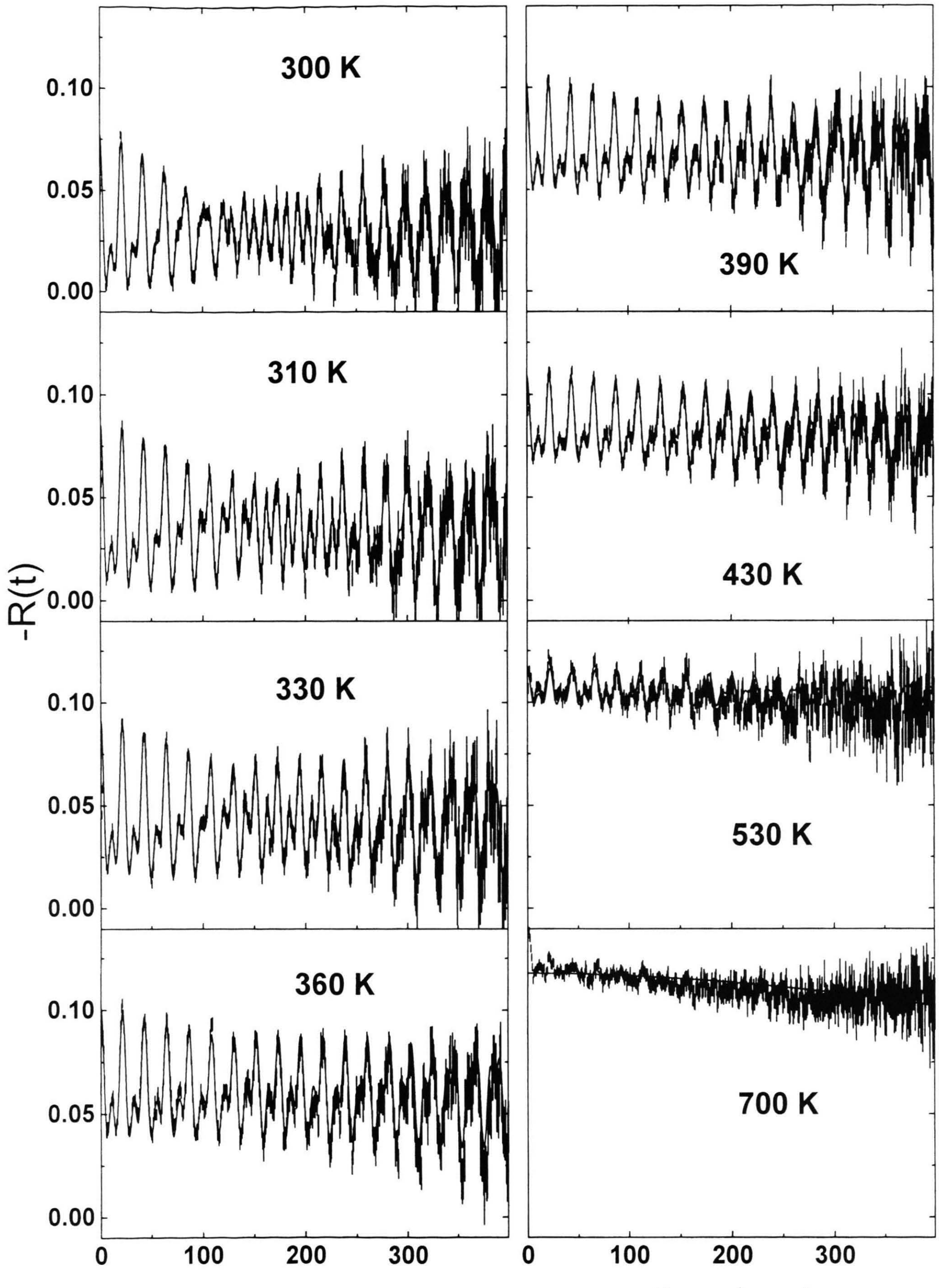

Fig. 1. Perturbation functions $-R(t)$ for $^{111}In/^{111}Cd$ in $SrTiO_3$ taken at $T = 300$ - 700 K. Note the beats which are due to the similarity of the two quadrupole frequencies ω_{Q1} and ω_{Q2} of the fractions f_1 and f_2.

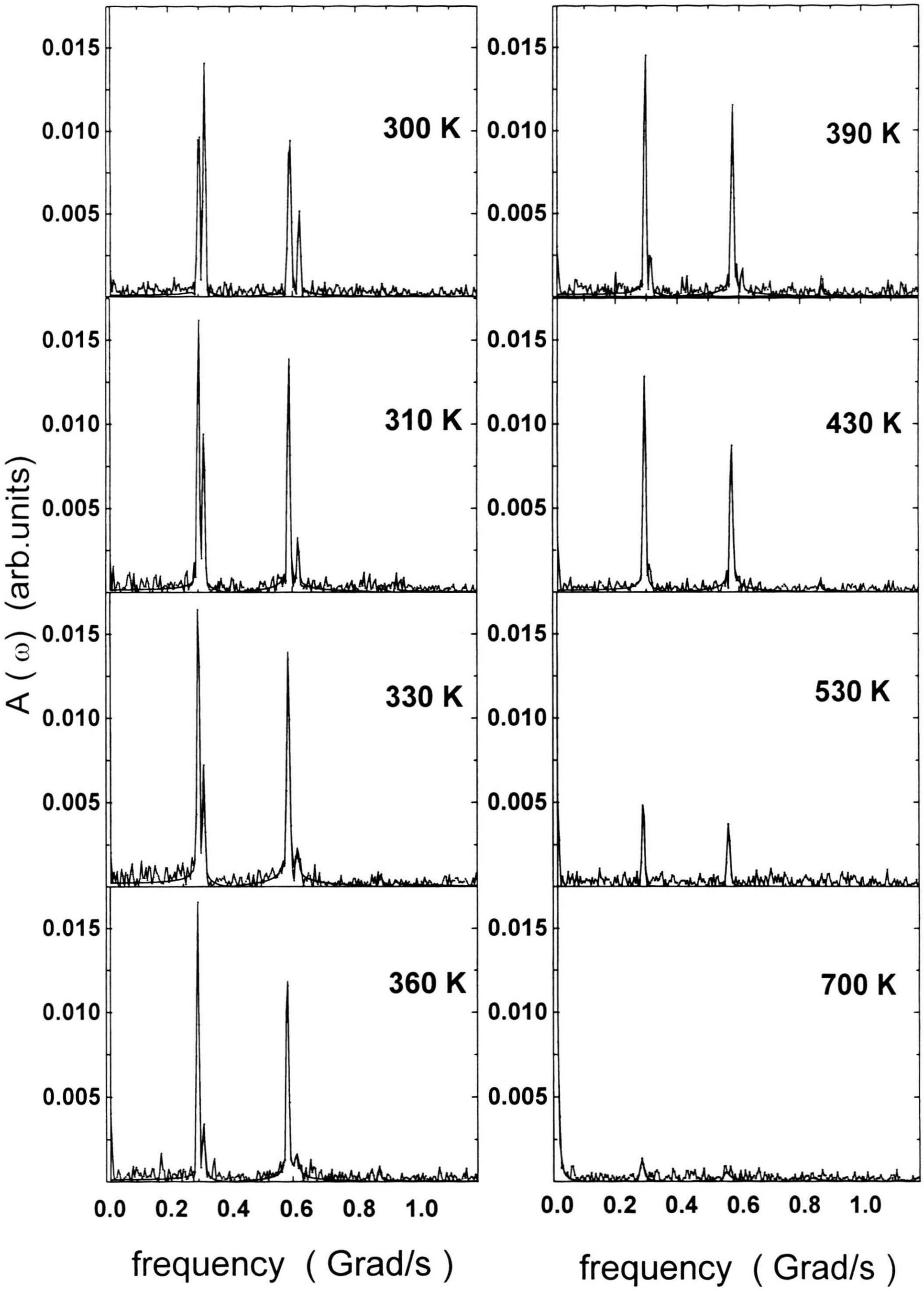

Fig. 2. Fourier transforms of the perturbation functions displayed in Figure 1.

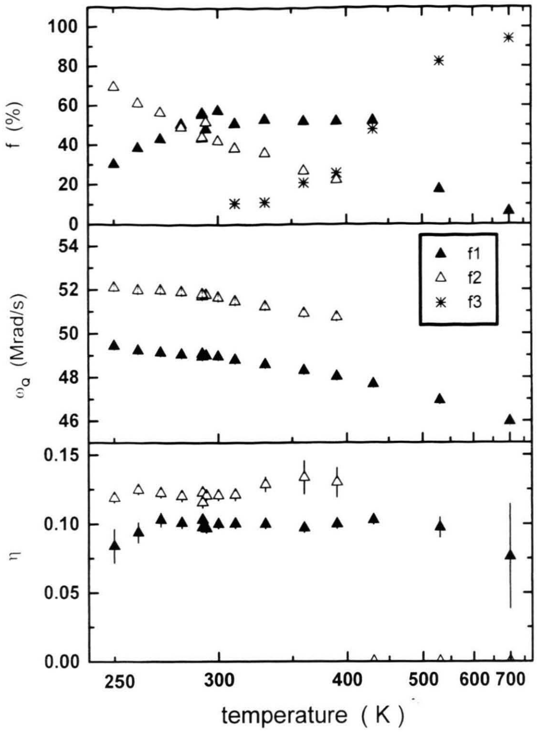

Fig. 3. Temperature dependence of the fractions f_i, quadrupole frequencies ω_{Qi} and asymmetry paramters η_i of the three hyperfine components $i = 0 - 2$.

air or high vacuum between 300 K and 700 K. Further details of the experimental set-ups used and data analysis can be found in [8, 10, 11].

3. Results

Figures 1 and 2 illustrate perturbation functions $R(t)$ and their Fourier transforms $A(\omega)$ taken between 300 and 700 K. At 700 K, the perturbation function shows a slight damping corresponding to a narrow distribution of quadrupole frequencies around ω_{Q0} = 0 Mrad/s. In the temperature interval from about 250 K up to 530 K, two well-defined EFG's are visible, characterized by the quadrupole frequencies and asymmetry parameters $\omega_{Q1} = 49.1(3)$ Mrad/s, $\eta_1 = 0.10(1)$, and $\omega_{Q2} = 51.8(3)$ Mrad/s, $\eta_2 = 0.12(1)$, respectively, at room temperature. Both EFG's are very well defined and have relative distribution widths of less than 1%.

The temperature dependences of the fractions f_i and parameters ω_{Qi} and η_i for all three EFG's in the range from 250 to 700 K are displayed in Figure 3. The cubic fraction f_0 sets in at about 300 K and reaches 100% at 700 K. The fraction f_2 steadily drops from f_2 = 70% at 250 K for increasing temperature, while the fraction f_1 reaches a flat maximum of 55% at 280 - 430 K and disappears around 700 K. All fractions were found to be independent on the pre-treatment of the samples, i. e. the changes are reversible. It is interesting to note that both ω_{Q1} and ω_{Q2} decrease linearly with the temperature, $\omega_{Qi}(T) = \omega_{Qi}(0) - b_i T$. The parameters are $\omega_{Q1}(0) = 51.3$ Mrad/s, $b_1 = 0.0079$ Mrad/sK and $\omega_{Q2}(0) = 54.8$ Mrad/s, $b_2 = 0.0106$ Mrad/sK, respectively. The PAC spectra taken below 100 K are strongly damped and their Fourier transforms exhibit a broad frequency peak centered around $\langle\omega_Q\rangle$ = 37 Mrad/s.

In order to determine the orientations of EFG_1 and EFG_2 relative to the crystal axes, we also accumulated PAC spectra at room temperature in a sample whose surface was cut along the $\{100\}$ plane and which was rotated around the surface normal direction lying in the detector plane. Writing the angular correlation function for a single EFG as

$$W(\boldsymbol{k}_1, \boldsymbol{k}_2, t) = 1 + A_2 \sum s_{2n}^{\text{eff}} \cos[g_n(\eta)\omega_0 t]$$

where $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ are the wavevectors of the two coincident γ-quanta, and neglecting the small A_4 term, the coefficients s_{2n}^{eff} depend on the orientation of the EFG tensor $\mathbf{V}_{jj}$ relative to the crystal lattice and the detectors' coordinate system. In the analysis, we followed the theoretical work by Wegner [12] for ^{111}Cd in single crystals which tabulates the coefficients s_{2n}^{eff} for $\eta = 0$ and $\eta = 0.2$. As the s_{2n}^{eff}-values vary very little in this interval of η, they can be well interpolated for the actual values of $\eta_1 \approx \eta_2 \approx 0.1$. Both EFG_1 and EFG_2 were found to be consistent with their main components $\mathbf{V}_{zz}$ pointing along the $\langle 100\rangle$ lattice direction.

4. Interpretation

On the basis of the cubic structure of $SrTiO_3$ one would expect a vanishing EFG for $^{111}In/^{111}Cd$ probe nuclei on unperturbed lattice sites. In all perovskite oxides studied so far [2, 7, 8], large fractions of such substitutional implantations have been identified. In the present work, the fraction f_0 rising with temperature up to 100% at 700 K obviously is a good candidate for this environment. The chemical valency of $^{111}In^{3+}$ and similar PAC results for ^{111}In or ^{181}Hf

tracers in the other perovskites strongly support the assumption that ^{111}In substitutes the 3+ cations, i. e. Ti, in $SrTiO_3$.

Figure 3 clearly indicates that at lower temperatures the hyperfine interaction evolves from the fraction f_2 to the fraction f_1 (both fractions having well-defined EFG's), before reaching the cubic site f_0. These transformations are reversible. Defect reactions in metals and semiconductors studied via PAC have shown similar behaviours of ^{111}In-defect complexes being formed and dissociating for increasing temperature. Among the point defects most probably oxygen vacancies are the predominant defect type as proposed by Wenzel et al. [13] in CoO and NiO. For ^{111}In in the binary oxides CrO_2, Ga_2O_3, ZrO_2, HfO_2 and La_2O_3, electronic defects have been made responsible for the appearance of additional EFG's [9, 11, 14, 15]. Electronic defects always led to variations of the hyperfine interaction fractions f_i, which are reversible with temperature. Since EFG_1 and EFG_2 have very narrow frequency widths δ_i at all temperatures and since the transformations occur in a fully reversible manner, we tend to assume that the ^{111}In-defect complexes in $SrTiO_3$ are of electronic nature. Their interpretation needs, however, further measurements, both using PAC and other methods such as conductivity and optical analysis.

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