

## Temperature dependence of electric field gradient in $\text{TbCoO}_3$

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**Abstract** The temperature dependence of the electric field gradient (efg) in  $\text{TbCoO}_3$  perovskite was measured by perturbed angular correlation (PAC) technique using  $^{111}\text{Cd}$  and  $^{181}\text{Ta}$  nuclear probes. The radioactive parent nuclei  $^{111}\text{In}$  and  $^{181}\text{Hf}$  were introduced into the compound through a chemical process during sample preparation. The electric quadrupole interactions at  $^{111}\text{Cd}$  show two different sites, assigned to probe substituting Tb and Co atoms. The temperature dependence of quadrupole frequencies show sharp discontinuities which have been interpreted as thermally activated spin state transitions from low-spin ground state configuration to the intermediate-spin state and from intermediate-spin to high-spin state of  $\text{Co}^{3+}$  ion. For  $^{181}\text{Ta}$  only one interaction was observed, which was assigned to probe at Co site. Indication of a Jahn–Teller distortion, which stabilizes the intermediate-spin state with orbital ordering, is also pointed out. No magnetic order was observed till 77 K.

**Keywords** Rare-earth oxides · PAC spectroscopy · Quadrupole interaction · Spin state transition

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### 1 Introduction

Perovskite oxides of the type  $\text{ABO}_3$ , where A is a rare-earth and B is Co, have been studied with particular interest because of their magnetic and electrical properties

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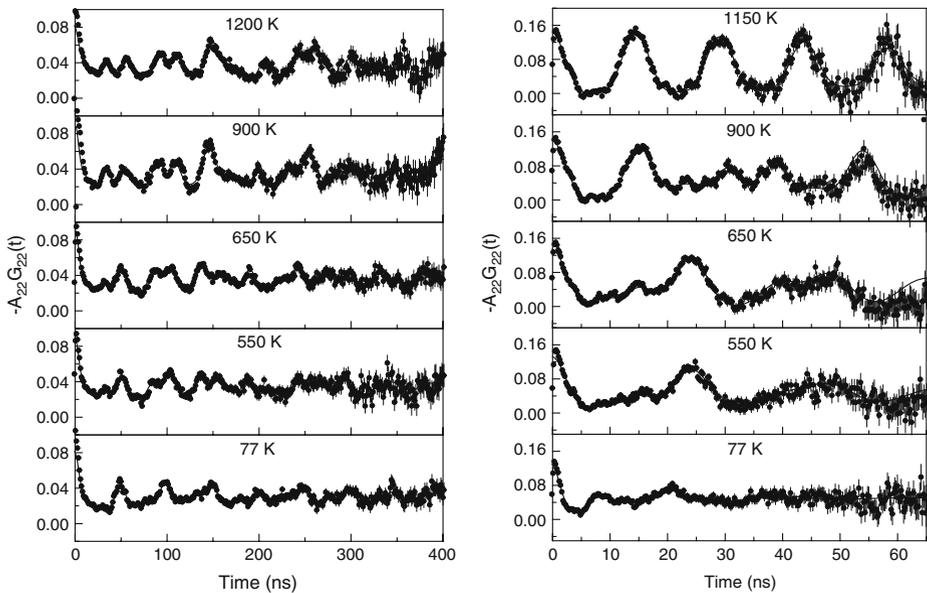
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that show an interesting behavior with temperature. In the perovskite structure, the A cation is coordinated with twelve oxygen ions and the B cation with six. Thus, the A cation is normally found to be somewhat larger than the B cation. The ideal cubic structure is, however, distorted by cation size mismatch and becomes orthorhombic or rhombohedral.  $\text{RCoO}_3$  perovskites show electronic phase transitions with change of temperature [1]. In last few years rare earth cobaltites have been extensively investigated and results show that the  $\text{LaCoO}_3$  presents a rhombohedral crystallographic structure and the other members of the family exhibit an orthorhombic structure. Special interest in the  $\text{LaCoO}_3$ , arises because of its peculiar and interesting magnetic and electric properties, due the Co cations. The  $\text{LaCoO}_3$  presents a magnetic insulator behavior in the ground state with configuration  $S=0$ ,  $t_{2g}^6$  (low spin, LS), undergoes a spin transition to  $S=2$ ,  $t_{2g}^4 e_g^2$  (high spin, HS). Recently, theoretical calculations as well as experimental work [2, 3] in  $\text{LaCoO}_3$  have reported that the transition from low to high spin configurations occurs through an intermediate spin state ( $t_{2g}^4 e_g^2$ ). Other  $\text{RCoO}_3$  perovskites exhibit an insulator to metal transition at 500–700 K, which was associated with a transition from the IS state to HS state [4, 5]. It would be therefore interesting to investigate other rare earth cobaltite using a sensitive local technique in order to search for spin transitions. In this work perturbed angular correlation (PAC) technique was used to study the temperature dependence of electric field gradient (efg) in  $\text{TbCoO}_3$  using  $^{111}\text{Cd}$  and  $^{181}\text{Ta}$  nuclear probes.

## 2 Experimental procedure

Samples of  $\text{TbCoO}_3$  were prepared from a mixture of Terbium nitrate  $\text{Tb}(\text{NO}_3)_3$  and cobalt nitrate  $\text{Co}(\text{NO}_3)_3$  solutions prepared by dissolving metallic Tb (99.9 %) and Co (99.99%) in concentrated  $\text{HNO}_3$ . Approximately 20  $\mu\text{Ci}$  of carrier free  $^{111}\text{In}$  and about 30  $\mu\text{Ci}$  of a  $^{181}\text{Hf}$  in dilute Hf solution were added to two different portions of the mixed nitrate solution. Each part was then slowly evaporated to dryness. The resulting powders were pressed into small pellets and sintered for 5 h at 1,300 K in air. The pellets were ground to a powder and sintered again at about 1,600 K for 5 h in air. The radioactive  $^{181}\text{Hf}$  was prepared by irradiating approximately 0.5 mg of Hf metal (99.9%) with thermal neutrons at the IEA-R1 research reactor at IPEN for about 30 h and then dissolved in a couple of drops of HF to obtain a dilute solution.

X-ray diffractometry was used to verify the crystal structure of the samples. The results indicate the presence of single  $\text{TbCoO}_3$  phase. The PAC technique was used to measure the quadrupole interaction in both samples of  $\text{TbCoO}_3$  doped with  $^{111}\text{Cd}$  and  $^{181}\text{Ta}$  probe nuclei using the well-known  $\gamma$ - $\gamma$  cascades of 171–245 keV and 133–482 keV, populated in the electron capture decay of  $^{111}\text{In}$  and  $\beta^-$  decay of  $^{181}\text{Hf}$  respectively. PAC spectra were recorded at several temperatures in the range of 77–1,200 K using a standard set up with four  $\text{BaF}_2$  detectors. A small tubular furnace was used for heating the samples with temperature controlled to within 1 K. For the measurement at 77 K, the samples were immersed in liquid nitrogen. Details of PAC data acquisition and analysis of quadrupole interaction in a polycrystalline sample are described in [6, 7].



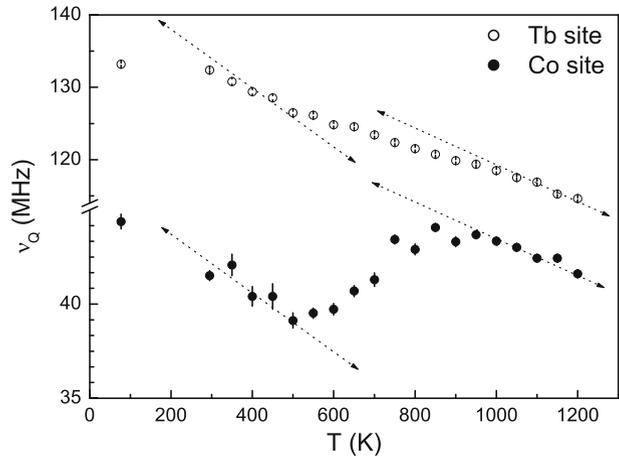
**Fig. 1** Perturbation functions with corresponding frequency spectra for  $^{111}\text{Cd}$  (left) and  $^{181}\text{Ta}$  probe nuclei (right) in  $\text{TbCoO}_3$  perovskite at various temperatures. Solid lines are the least squares fit of the theoretical function to the experimental data

### 3 Results and discussion

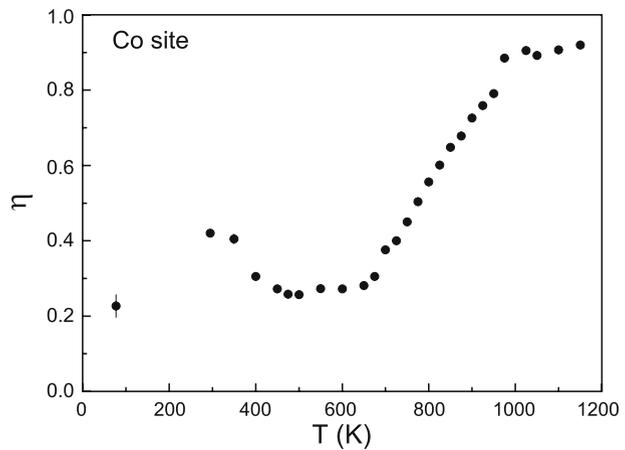
Some of the perturbation functions measured at different temperatures using  $^{111}\text{Cd}$  and  $^{181}\text{Ta}$  probes, are shown in Fig. 1. The PAC spectra were least square fitted in both cases using appropriate theoretical perturbation function [6]. The fitted curves are shown in the figures as solid lines. Results of the measurements carried out with  $^{111}\text{Cd}$  probe show two fractions with well-resolved quadrupole interaction at all temperatures. The observed quadrupole frequencies at 77 K  $\nu_Q = 133(1)$  MHz ( $\eta = 0.14$ ) and  $\nu_Q = 44.4(4)$  MHz ( $\eta = 0.47$ ) were associated to  $^{111}\text{Cd}$  probe nuclei at Tb and Co sites, respectively. This assignment is based on results of previous PAC results for several rare-earth perovskites [4, 6, 8]. The measurements with  $^{181}\text{Ta}$  probe showed a single fraction with well-resolved quadrupole interaction, which was associated to  $^{181}\text{Ta}$  at Co sites. Once again this assignment is based on the previous PAC study of  $\text{LaCoO}_3$  [4]

The temperature dependence of the quadrupole frequencies ( $\nu_Q$ ) for  $^{111}\text{Cd}$  at both Tb and Co sites show discontinuities at three different temperature regions from around 300–500 K, 500–900 K and above 900 K, as seen in Fig. 2. These discontinuities are seen more clearly for the data taken with  $^{111}\text{Cd}$  probe at Co sites. Similar discontinuities were also observed in PAC measurements in  $\text{LaCoO}_3$  [4] and were attributed to thermally induced spin state transition in Co atoms from low-spin (LS) nonmagnetic state ( $t_{2g}^6 e_g^0$ ) to an intermediate-spin (IS) state ( $t_{2g}^5 e_g^1$ ) and then from the intermediate-spin (IS) state to high-spin (HS) state ( $t_{2g}^4 e_g^2$ ) respectively. In the present case transition from LS or IS state to HS state was observed in a wide

**Fig. 2** Temperature dependence of the fitted quadrupole frequencies  $\nu_Q$  corresponding to  $^{111}\text{Cd}$  probes at Tb (open circles) and Co sites (full circles) in  $\text{TbCoO}_3$  perovskite



**Fig. 3** Temperature dependence of the fitted asymmetry parameter  $\eta$  and quadrupole frequencies  $\nu_Q$  for  $^{181}\text{Ta}$  probes at Co sites in  $\text{TbCoO}_3$  perovskite



range of temperature from 500 to 900 K, in other words  $\text{Co}^{3+}$  in  $\text{TbCoO}_3$  is at LS or IS site below 500 K and at HS state above 900 K. The LS to IS transition is not sharp.

The quadrupole frequencies at  $^{111}\text{Cd}$  substituting Tb as well as Co sites decrease almost linearly above  $\sim 295$  K with increasing temperature, except in the region from 500 to 850 K, where the values increase. For both Tb and Co sites, the slope of the curves for the linear decrease is almost the same before and after the discontinuity around 700 K, as shown in Fig. 2. Since the electric quadrupole interaction at the probes substituting Co sites results mainly from the six surrounding  $\text{O}^{2-}$  ions forming an octahedron, a general increase in all the bond lengths resulting from thermal expansion of the crystal lattice is expected to reduce the quadrupole frequencies. However, at around 500–850 K, where the LS–IS and IS–HS transitions take place, one can observe a sudden increase in the quadrupole frequencies. In this temperature regions the spin-state transition provokes a sudden increase in the Co ionic radius, which results in an increase in the Co–O bond length. As a consequence, the O

atoms are pushed towards the probe atoms. Reduced O-probe distance produces an increase in the quadrupole frequency.

In the case of measurements carried out with  $^{181}\text{Ta}$  probe, values of  $\eta$  decrease some what from 200 to 475 K, and then increase sharply till the highest temperature of measurement as shown in Fig. 3. For example, at 295 K  $\eta = 0.42$  and  $\nu_Q = 359.7$  MHz. This value for  $\nu_Q$  is about seven times higher than the value for  $^{111}\text{Cd}$  at same temperature. The values of  $\nu_Q$  show a very weak temperature dependence above 350 K. The interpretation of this behavior is the following: between 295 to 475 K the  $\text{Co}^{3+}$  ions are at LS state, in the temperature range 475–650 K, we believe that Co ions change to IS state and at still higher temperature they change to HS state. This behavior is ascribed to the doping of the sample with Hf, which although being small (0.1%) is enough to perturb the spin state properties of the Co ions in this compound. We suggest that this perturbation results in a Jahn–Teller distortion in the local structure that induces a mixed spin states of cobalt ions.

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