

Spin transitions of Co ions in RCoO_3 (R=Gd,Tb) investigated by measuring the electric field gradient at R and Co sites

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Hyperfine interactions in perovskite-structure RCoO_3 (R=Gd,Tb) compounds have been measured by perturbed angular correlation technique using ^{111}Cd and ^{181}Ta nuclear probes. The electric quadrupole interactions at ^{111}Cd show two different sites, assigned to probe substituting Gd or Tb and Co atoms. The temperature dependence of quadrupole frequencies shows discontinuities which have been interpreted as thermally activated spin-state transitions from low-spin ground state configuration to the intermediate-spin (IS) state and from IS state to high-spin state of Co^{3+} ion. For ^{181}Ta only one major interaction was observed, which was assigned to probe at Co sites. Indication of a Jahn-Teller distortion, which stabilizes the intermediate-spin state with orbital ordering, is also pointed out. © 2008 American Institute of Physics. [DOI: [10.1063/1.2835066](https://doi.org/10.1063/1.2835066)]

I. INTRODUCTION

RCoO_3 compounds where R is a rare-earth element are found to exhibit interesting electronic properties that change with temperature.¹ These compounds have the perovskite-type structure which is characterized as a cubic close-packed array of oxygen anions and large rare-earth cations with small transition metal cations occupying the octahedral interstitial sites. This ideal cubic structure is, however, distorted by cation size mismatch and becomes orthorhombic or rhombohedral. In RCoO_3 family, LaCoO_3 presents a rhombohedral crystallographic structure and the other members exhibit an orthorhombic structure. Rare-earth cobaltites have been extensively investigated and results show that cobalt ions with six d electrons in an octahedral coordination can be either in a low-spin (LS) state ($t_{2g}^6 e_g^0$) or in a high-spin (HS) state ($t_{2g}^4 e_g^2$) depending on the temperature. RCoO_3 perovskites exhibit an insulator to metal transition at 500–700 K, which was associated with the spin transition.² More recently, theoretical calculations as well as experimental work^{3,4} in LaCoO_3 have reported that the transition from low- to high-spin configurations occurs through an intermediate-spin (IS) state ($t_{2g}^5 e_g^1$). It would be therefore interesting to investigate other rare-earth cobaltites using a very sensitive local technique in order to search for an intermediate state. In this work perturbed angular correlation (PAC) technique was used to study the temperature dependence of electric field gradient (efg) in GdCoO_3 and TbCoO_3 using ^{111}Cd and ^{181}Ta nuclear probes.

II. EXPERIMENTAL PROCEDURE

Samples of RCoO_3 (R=Gd,Tb) were prepared from a mixture of rare-earth nitrate $\text{R}(\text{NO}_3)_3$ and cobalt nitrate $\text{Co}(\text{NO}_3)_3$ solutions prepared by dissolving metallic Gd(Tb) (99.9%) and Co (99.99%) in concentrated HNO_3 . Both ni-

trate solutions were mixed to obtain a homogeneous aqueous solution. Approximately 20 μCi of carrier free ^{111}In and about 30 μCi of a ^{181}Hf in dilute Hf solution were added to two different portions of the mixed nitrate solution of each compound. Each mixture was then slowly evaporated to dryness. The resulting powders were sintered for 5 h at 1400 K in air. The powders were pressed into small pellets and sintered again at about 1400 K for 10 h in air. The radioactive ^{2181}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 indicated the presence of single phase for both compounds. The PAC technique was used to measure the quadrupole interaction in each compound with ^{111}Cd and ^{181}Ta as probe nuclei. The well-known γ - γ cascades of 171–245 and 133–482 keV, populated in the electron capture decay of ^{111}In and β^- decay of ^{181}Hf , respectively, were used to measure the quadrupole interaction of the 245 keV ($5/2^+$) spin state of ^{111}Cd and the 482 keV ($5/2^+$) spin state of ^{181}Ta . PAC spectra were recorded at several temperatures in the range of 10–1200 K using a standard setup with four BaF_2 detectors.⁵ A small tubular furnace was used for heating the samples with temperature controlled to within 1 K. For low temperature measurements the sample was attached to the cold finger of a closed-cycle-helium refrigerator with temperature controlled to better than 0.1 K. Details of PAC data acquisition and analysis of quadrupole interaction in a polycrystalline sample are described in Refs. 5 and 6

The PAC method is based on the observation of hyperfine interaction of nuclear moments with extranuclear magnetic fields (B_{hf}) or an electric field gradient. The technique measures the time evolution of the γ -ray emission pattern caused by hyperfine interactions. A description of the method as well as details about the PAC measurements can be found

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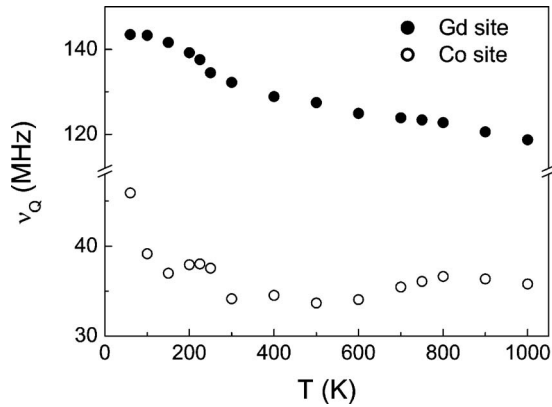


FIG. 1. Temperature dependence of the quadrupole frequencies ν_Q corresponding to ^{111}Cd probes at Gd (open circles) and Co sites (full circles) in GdCoO_3 perovskite.

else where.^{5,7} The perturbation factor $G_{22}(t)$ of the correlation function contains detailed information about the hyperfine interaction. Measurement of $G_{22}(t)$ allows the determination of the Larmor frequency $\omega_L = \mu_N g B_{\text{hf}} / \hbar$, the nuclear quadrupole frequency $\nu_Q = eQV_{zz}/h$, as well as the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx} , V_{yy} , and V_{zz} are the components of the efg tensor in its principal axis system. Consequently, from the known quadrupole moment Q of the 245 keV state of ^{111}Cd and the 482 keV state of ^{181}Ta the major component V_{zz} of efg and its asymmetry parameter η can be determined.

III. RESULTS AND DISCUSSION

Results of the measurements carried out with ^{111}Cd probe show two fractions with well-resolved quadrupole interaction at all temperatures for each compound. The observed higher and lower quadrupole frequencies were assigned to ^{111}Cd probe nuclei at R and Co sites, respectively. This assignment is based on results of previous PAC results for several rare-earth perovskites.^{4,5,8} The measurements with ^{181}Ta probe showed a major fraction with well-resolved quadrupole interaction, which was associated to ^{181}Ta at Co sites and a minor fraction which vanishes at temperatures higher than 850 K with wide frequency distributions. Once again this assignment is based on the previous PAC study of LaCoO_3 .⁴

The temperature dependence of the quadrupole frequency (ν_Q) for ^{111}Cd at both Gd and Co sites shows a discontinuity in the region from around 200 to 250 K, as seen in Fig. 1. A second discontinuity is seen in the region from 600 to 750 K, which is more clearly observed for the data taken with ^{111}Cd probe at Co sites. The observed quadrupole frequencies ν_Q for the Gd and Co sites, for example, are 127(1) and 34.5(3) MHz at 500 K and 122(1) and 36.6(3) MHz at 800 K.

The temperature dependence of ν_Q , shown in Fig. 2 for ^{111}Cd at both Tb and Co sites for TbCoO_3 , also shows discontinuities at two different temperature regions at around 300 K and in the region from 650 to 800 K. As before these discontinuities are better seen for data taken at Co sites. Similar discontinuities were also observed earlier in the mag-

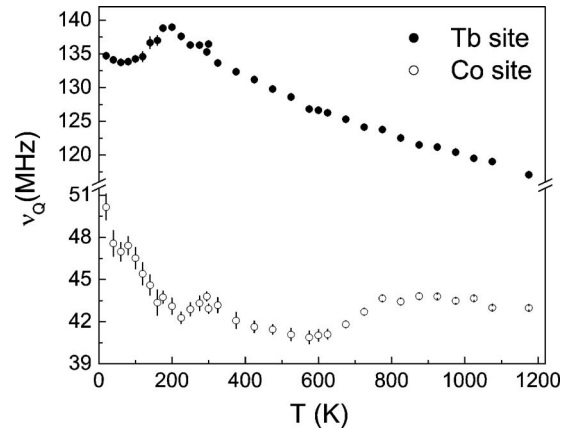


FIG. 2. Temperature dependence of the quadrupole frequencies ν_Q corresponding to ^{111}Cd probes at Tb (open circles) and Co sites (full circles) in TbCoO_3 perovskite.

netic susceptibility data⁹ and in PAC measurements in LaCoO_3 (Ref. 4) and were attributed to thermally induced spin-state transition in Co atoms from LS nonmagnetic state ($t_{2g}^6 e_g^0$) to an IS state ($t_{2g}^5 e_g^1$) and then from the IS state to the HS state ($t_{2g}^4 e_g^2$), respectively.

The quadrupole frequencies at ^{111}Cd substituting Gd or Tb as well as Co sites decrease almost linearly above ~ 300 K with increasing temperature, except in the transition regions where the values increase. For both Gd(Tb) and Co sites the slope of the curves for the linear decrease is almost the same before and after the discontinuities. Since the electric quadrupole interaction at the probes substituting Co sites results mainly from the six surrounding 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, where the LS-IS and IS-HS transitions take place, one can observe a sudden increase in the quadrupole frequencies. In these 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 toward the probe atoms. Reduced O–probe distance produces an increase in the quadrupole frequency.

In the case of measurements carried out with ^{181}Ta probe, values of η decrease somewhat for temperatures higher than 200 and 300 K, respectively, for GdCoO_3 and TbCoO_3 and then increase sharply until the highest temperature of measurement. The values of ν_Q show a very weak temperature dependence above 350 K. The interpretation of this behavior is the following: between 295 and 475 K the Co^{3+} ions are at LS state; in the temperature range of 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 mixed spin states of cobalt ions.

Although LaCoO_3 has a rhombohedral crystal structure and (Gd, Tb) CoO_3 have orthorhombic structure, one can observe that the transition temperatures from LS to IS and from

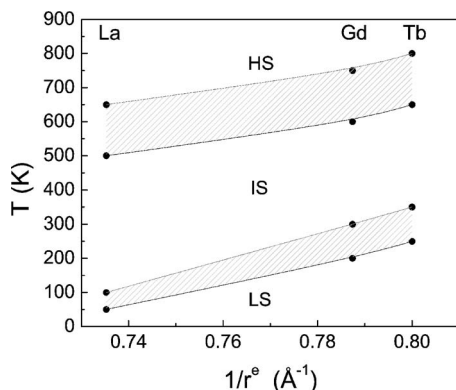


FIG. 3. Temperature range for spin transition in Co ions for LaCoO₃, GdCoO₃, and TbCoO₃ cobaltites as a function of the inverse of effective ionic radius of the rare-earth ion for 12 coordinations taken from Ref. 10. The dashed areas are only visual guides and represent the transition temperature regions.

IS to HS spin states of Co ions in TbCoO₃ and GdCoO₃ when compared to LaCoO₃, also determined with PAC measurements,⁴ are roughly proportional to the inverse of the effective ionic radius of the rare-earth ion in an environment with 12 coordinations, respectively, 1.25, 1.27, and 1.36 Å, taken from Ref. 10 as shown in Fig. 3. This observation can be explained by the fact that the crystalline electric field, responsible for the molecular orbital splitting, will be higher when the cell volume is smaller and as a consequence the level splitting will be higher thus requiring higher temperature to promote electrons from one energy level to a higher energy level.

IV. SUMMARY

In the present work, the quadrupolar interaction at R and Co sites in RCoO₃ (R=Gd, Tb) compounds measured with perturbed γ - γ angular correlation spectroscopy using ¹¹¹Cd and ¹⁸¹Ta nuclear probes is reported. The results for the temperature dependence of (ν_Q) at ¹¹¹Cd and ¹⁸¹Ta sites show

significant discontinuities in two different regions of temperatures for both compounds. These discontinuities were attributed to thermally induced spin-state transition in Co atoms from LS nonmagnetic state ($t_{2g}^6 e_g^0$) to IS state ($t_{2g}^5 e_g^1$) and then from the IS state to the HS state ($t_{2g}^4 e_g^2$). The temperature regions where these discontinuities take place are higher than those for LaCoO₃. These temperature regions together with those previously reported by LaCoO₃ also determined with PAC measurements are shown to be proportional to the inverse of the effective ionic radius of the rare-earth ion. These results are believed to be an effect of the crystalline electric field.

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