

Measurement of Quadrupole Interactions in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ Perovskites Using TDPAC Technique

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Abstract. The Perturbed Angular Correlation (PAC) technique was used to study the quadrupole interactions in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 \leq x \leq 0.08$) perovskites using ^{111}Cd and ^{181}Ta probes. The radioactive parent nuclei ^{111}In and ^{181}Hf were introduced in the oxide lattice through chemical process during sample preparation and found to occupy only Co sites. The measurements cover a temperature range from 10 to 1150 K except the pure LaCoO_3 for which an additional measurement was made at 4.2 K. The measured quadrupole frequencies were found to decrease linearly with increasing temperature as well as with increasing Sr concentration. Temperature dependence of quadrupole frequency in the pure LaCoO_3 shows small discontinuities around 70–90 K and 500–600 K which have been attributed to thermally activated spin state transitions, from the low-spin (LS) ground state electronic configuration of Co^{+3} ion to the intermediate-spin (IS) state and from intermediate-spin (IS) state to high-spin (HS) state respectively, observed in some recent studies.

Key Words: electric field gradient, magnetism, metallic oxides, PAC spectroscopy.

1. Introduction

Perovskite oxides of 3d transition metal of the type LnMO_3 , where Ln is a rare-earth element, are found to exhibit a variety of unusual and interesting transport, magnetic and structural properties. The structure of a perovskite oxide 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. The ideal cubic structure is, however, distorted by cation size mismatch and becomes orthorhombic or rhombohedral. The perovskite compound LaCoO_3 , which crystallizes in a rhombohedrally-distorted structure with

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$R\bar{3}C$ symmetry, has attracted special attention in the past few decades because of the peculiar way its electronic and magnetic properties change with temperature [1].

The ground state electronic spin configuration of the LaCoO_3 is low-spin (LS) ($t_{2g}^6 e_g^0$) state at low temperatures. The broad transition in the magnetic susceptibility observed at 90–100 K corresponds to the thermal activation of an excited state which could be either a high spin (HS) ($t_{2g}^4 e_g^2$) or an intermediate spin (IS) ($t_{2g}^5 e_g^1$) configuration. Several studies provided evidence to support one transition type over the other. The majority of new results however point towards the sequence $\text{LS} \rightarrow \text{IS} \rightarrow \text{HS}$ with increasing temperature [2, 3] particularly in view of a second transition observed in the magnetic susceptibility at ~ 500 – 600 K corresponding to the population of HS state. Substitution of Sr^{2+} for La^{3+} in LaCoO_3 brings about significant changes in the system [4, 5]. The introduction of the larger Sr^{+2} cation progressively reduces the rhombohedral distortion present in the parent LaCoO_3 compound and suppresses the transition to LS state while stabilizing the IS state. For values of $x \geq 0.18$, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ becomes ferromagnetic. It is expected therefore that a change in the spin state of cobalt as well as the reduced rhombohedral distortion in going from pure to doped compound would result in a corresponding change in the octahedral Co–O bond length. A detailed study of these perovskites with some suitable microscopic technique using an appropriate probe at Co site could reveal important information on the electronic properties including observed LS to IS and IS to HS state transitions observed in LaCoO_3 .

We have investigated the temperature dependence of quadrupole interaction in a series of perovskite oxides $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 \leq x \leq 0.08$) with TDPAC technique using ^{111}Cd and ^{181}Tm probe nuclei.

2. Experimental

Stoichiometric polycrystalline samples of pure and strontium doped oxides were prepared from a mixture of $\text{La}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$ solutions to which approximately 20–30 μCi of carrier free ^{111}In in the form of indium chloride solution or ^{181}Hf in the form of hafnium fluoride solution was added. The radioactive ^{181}Hf obtained by irradiating 1 mg of Hf metal with neutrons in the IEA-R1 reactor at IPEN for ~ 60 h in a flux of $2 \times 10^{13} \text{ n.cm}^{-1} \cdot \text{s}^{-1}$ was dissolved in dilute HF acid to obtain HfF_4 solution. In each case the mixture was slowly evaporated to dryness and the resulting powder was pressed in to small pellet, which was sintered for about 5 hours at 1000°C in air. The pellet was ground and sintered again for 5 hours at 1300°C in air. The samples were analyzed by powder x-ray diffraction method and found to be in single phase.

The TDPAC measurements were carried out in a conventional fast-slow coincidence set-up with four conical BaF_2 detectors generating 12 delayed coincidence spectra simultaneously. Gamma cascade of 133–482 keV populated

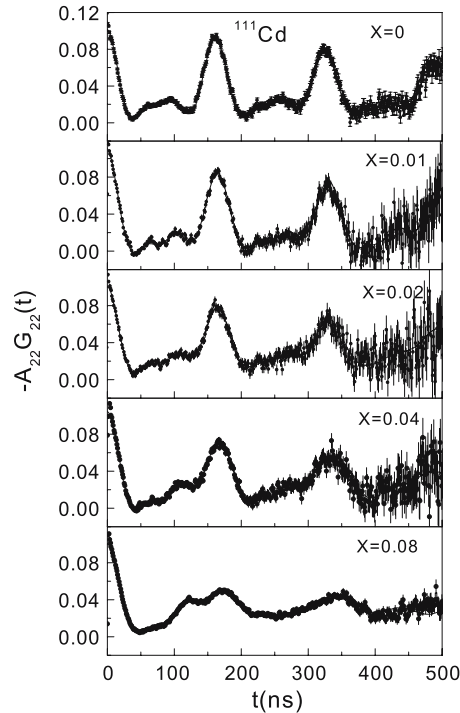


Figure 1. TDPAC spectra of ^{111}Cd for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ at different concentration of Sr.

in the β^- decay of ^{181}Hf and 172–245 keV cascade populated in the electron capture decay of ^{111}In was used to measure the quadrupole interaction of the 482 keV state of ^{181}Ta and 245 keV state of ^{111}Cd respectively. The time resolution of the system was about 700 ps. The samples were measured in the temperature range of 4.2–1150 K. A tubular furnace was used for heating the sample above room temperature. For low temperature measurements the samples were attached to the cold finger of a closed-cycle-helium cryostat. The measurement at 4.2 K was made by immersing the sample in liquid helium.

3. Results and discussion

Room temperature PAC spectra for some of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ compounds measured at different concentrations of Sr using ^{111}Cd probe are shown in Figure 1 as an example. For ^{111}Cd as well as the ^{181}Ta probe a sharp and well-defined quadrupole frequency was observed for samples with smaller concentrations of Sr and assigned to the probes occupying Co sites. These assignments are essentially based on the results of previous PAC studies with similar perovskites [6, 7]. In both cases a second interaction involving a minor fraction of probe nuclei was observed, which was attributed to some defects in the crystal structure. The quadrupole frequencies in both cases showed increasingly high distribution

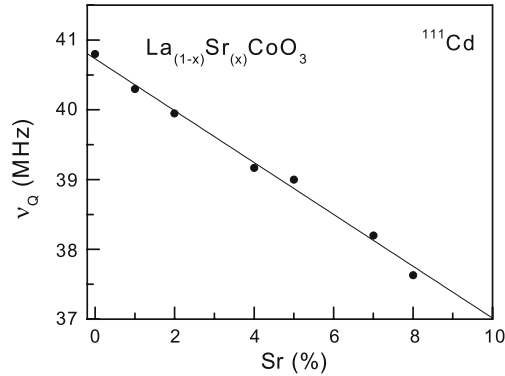


Figure 2. Quadrupole frequencies at room temperature as a function of Sr concentration.

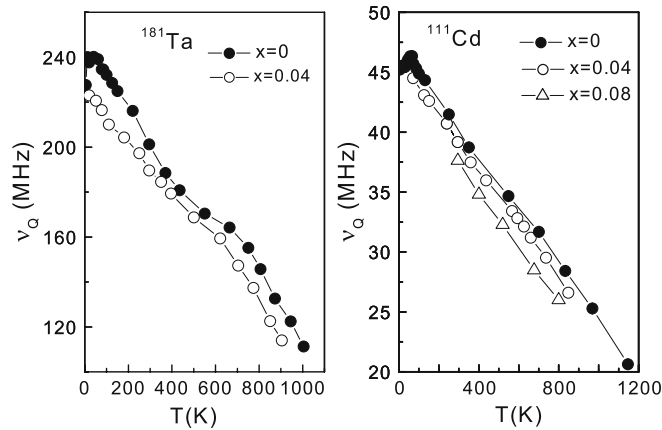


Figure 3. Temperature dependence of quadrupole frequency for pure and Sr doped LaCoO_3 determined with ^{111}Cd and ^{181}Ta probes.

at higher concentrations of Sr due to increasing disorder in the compound. As a consequence for Sr concentration greater than 8% it was no longer possible to determine the quadrupole frequencies accurately.

At all temperatures the quadrupole frequencies are found to decrease almost linearly with increasing Sr concentration (Figure 2). The quadrupole frequencies are also found to decrease almost linearly with increasing temperature for the doped as well pure samples. A closer look at the temperature dependence of quadrupole interaction frequencies however shows some important differences between the pure and Sr doped samples, in particular at higher Sr concentration ($x \geq 0.04$) (see Figure 3). The measurements carried out using ^{181}Ta as well as ^{111}Cd on pure LaCoO_3 sample show a peak like structure around 70–90 K. A second discontinuity is seen at about 500–600 K, which is barely visible in the case of ^{111}Cd but clearly observed for the data taken with ^{181}Ta probe. Similar discontinuities have been observed earlier in the magnetic susceptibility data as a

function of temperature. This behavior is compatible with the idea of a thermally induced spin transition from low-spin (LS) nonmagnetic state ($t_{2g}^6 e_g^0$) at around 70–90 K 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 ($t_{2g}^4 e_g^2$) at around 500–600 K reported for Co atoms in this compound [3]. With the Sr doping these discontinuities in the linear behavior of efg disappear.

Doping with Sr tends to stabilize the intermediate spin state at lower concentration and therefore the peak at 70–90 K is absent for this compound for $x = 0.04$. The IS to HS transition, however, continues as a function of temperature and the second discontinuity at about 500–600 K is still seen, particularly in the case of measurement with ^{181}Ta (see Figure 3). At still higher Sr concentration ($x \geq 0.08$) the temperature dependence is practically linear and the second peak also disappears. The present experiments with Sr doped LaCoO_3 perovskite thus show that the respective spin state transitions are sensitive to Sr concentration and for doping concentration of $x \geq 0.08$ the transition to HS configuration of Co^{+3} ions is almost complete. It is known that for $x \geq 0.18$ $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ becomes ferromagnetic [5].

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