

Investigation of spin transition in GdCoO_3 by measuring the electric field gradient at Co sites

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Abstract

In the present work, the time differential perturbed angular correlation (PAC) technique was used to study the temperature dependence of electric field gradient (efg) in GdCoO_3 perovskite using ^{111}Cd and ^{181}Ta nuclear probes. The radioactive parent nuclei ^{111}In and ^{181}Hf were introduced in the oxide lattice through chemical process during sample preparation and were found to occupy only the Co sites in GdCoO_3 . The efg's at ^{111}Cd and ^{181}Ta show temperature dependence with two different fractions each that change with temperature. In the case of ^{111}Cd the quadrupole frequency slowly decreases, with corresponding increase of the temperature and shows a peak like structure at around 200 K and a discontinuity at 700 K. These changes 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 Co^{3+} ion similar to LaCoO_3 compound. Indication of a Jahn–Teller distortion, which stabilizes the intermediate-spin state with orbital ordering, is also pointed out.

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1. Introduction

Perovskite oxides of 3d Co metal of the type RCoO_3 , where R is a rare-earth (RE) element, are found to exhibit interesting magnetic and electrical properties that vary with temperature. The structure of a perovskite oxide is characterized as a cubic close-packed array of oxygen anions and large RE 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. Extensive investigations on such compounds in last decades have shown that cobalt ions with six d-electrons in an octahedral coordination can be in either 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. Recently, theoretical calculations followed by experimental works [1,2] in

LaCoO_3 have reported that the transition from low to HS configurations occurs through an intermediate-spin (IS) state ($t_{2g}^5 e_g^1$). Therefore, it would be interesting to perform an investigation in other compounds of this family using a very sensitive local technique in order to search for an intermediate state. In the present work, the time differential perturbed angular correlation (TDPAC) technique was used to study the temperature dependence of electric field gradient (efg) in GdCoO_3 perovskite using ^{111}Cd and ^{181}Ta nuclear probes.

2. Experimental

Polycrystalline samples of GdCoO_3 were prepared from a mixture of Gadolinium nitrate $\text{Gd}(\text{NO}_3)_3$ and cobalt nitrate $\text{Co}(\text{NO}_3)_3$ solutions. Both $\text{Gd}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_3$ solutions were prepared by dissolving known quantities of metallic Gd (99.9%) and metallic Co (99.99%), respectively, in concentrated HNO_3 . Both nitrate solutions were

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mixed to obtain a homogeneous aqueous solution. Approximately 20 μCi of carrier free ^{111}In was added and the whole solution was slowly evaporated to dryness. The resulting powder was pressed into small pellets and sintered for 5 h at 1300 K in air. The pellets were ground to a powder and sintered again at about 1600 K for 5 h in air. The radioactive ^{181}Hf probe was introduced in the GdCoO_3 sample using a similar procedure. Approximately 1 mg of Hf metal (99.9%) was irradiated 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. About 30 μCi of this solution containing ^{181}Hf was added to the mixture of $\text{Gd}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_3$ solutions which was dried and sintered as described above.

The powder samples of GdCoO_3 were analyzed by the X-ray diffraction method to verify the crystal structure and presence of any contaminating phase. The PAC technique was used to measure the quadrupole interaction in the polycrystalline sample of GdCoO_3 using ^{111}Cd and ^{181}Ta probe nuclei. PAC method is based on the hyperfine interaction of nuclear moments with extra nuclear magnetic fields or efg's. In the case of quadrupolar electric interaction, the experimental measurement gives the quadrupolar frequency ν_Q with respective distribution δ as well as the efg asymmetry parameter η . A detailed description of this method can be found in Ref. [3]. 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 . TDPAC spectra were recorded at several temperatures using a standard set up with four BaF_2 detectors [4]. The PAC measurements were carried out in the temperature range of 50–1000 K for both probe nuclei. No magnetic order was observed up to 50 K. A small tubular furnace was used for heating the sample above room temperature, which was 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. [4,5].

3. Results and discussion

Some of the perturbation functions measured at different temperatures using ^{111}Cd and ^{181}Ta probes are shown in Figs. 1 and 2, respectively. The PAC spectra were least square fitted in both cases using appropriate theoretical perturbation function [4]. The fitted curves are shown in the figures as solid lines. Results of the measurements carried out with ^{111}Cd probe show two fractions with well-resolved quadrupole interaction at all temperatures. It was associated the observed higher and lower quadrupole frequency $\nu_Q = 143(1)\text{MHz}$ (fraction of 15%, $\eta = 0.46$)

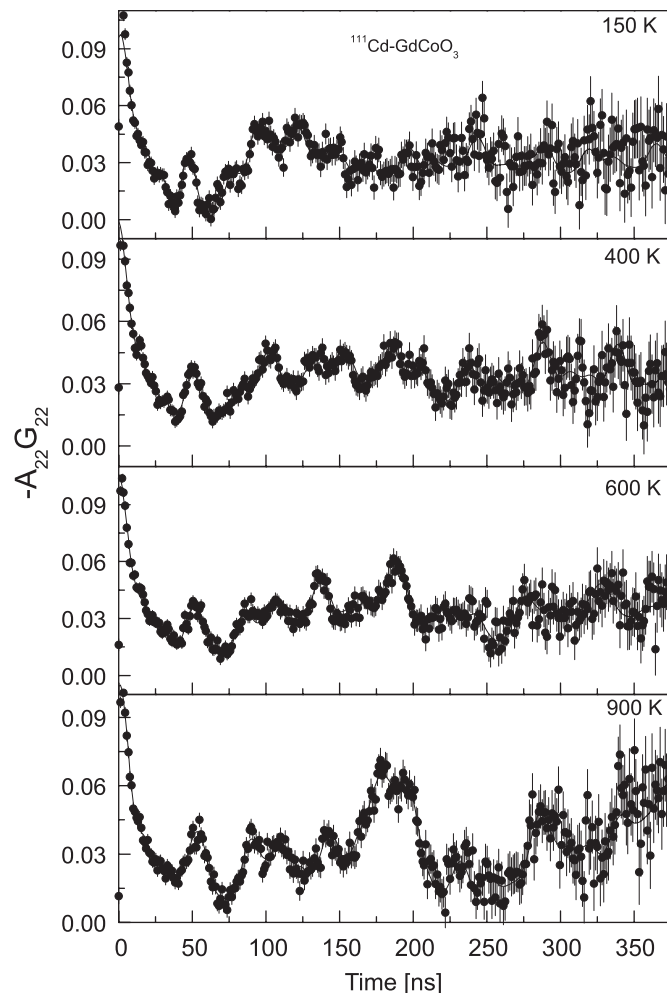


Fig. 1. Perturbation functions with corresponding frequency spectra for ^{111}Cd probe nuclei in GdCoO_3 perovskite at various temperatures. Solid lines are the least squares fit of the theoretical function to the experimental data.

and $\nu_Q = 39.2(4)\text{MHz}$ (fraction of 85%, $\eta = 0.44$) to ^{111}Cd probe nuclei at Gd and Co sites, respectively, at 100 K. This assignment is essentially based on the result of earlier PAC measurements in several RE perovskites [4,6] and in LaCoO_3 compound [2]. The $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ probe was introduced in these compounds by a similar chemical process as in the present study and while the first two works showed that the probe atoms can substitute both the RE as well as the transition metal sites, the later showed that ^{111}Cd substitute only Co sites. The measurements with ^{181}Ta probe also show two fractions with well-resolved quadrupole interaction that have close together values at all temperatures. Also based on previous PAC measurements in LaCoO_3 [2] both fractions were associated to probe at Co sites.

The temperature dependence of the quadrupole frequency (ν_Q) for ^{111}Cd at both Gd and Co sites shows a wide peak like structure in the region from around 100 K to 200 K, as seen in Fig. 3. A second discontinuity is seen at about 700 K, which is more clearly observed for the data

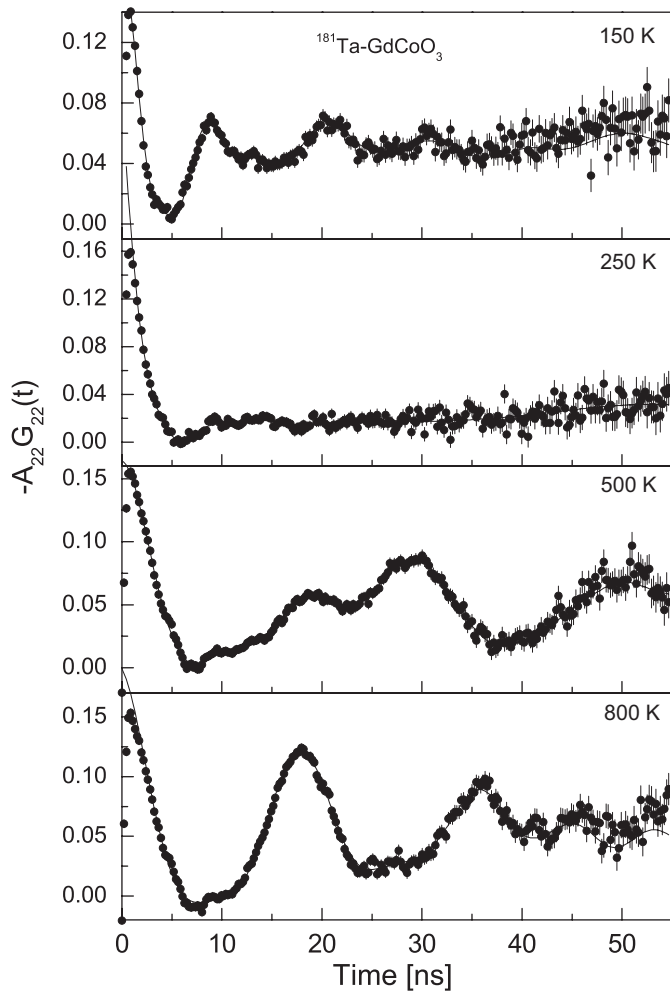


Fig. 2. Perturbation functions with corresponding frequency spectra for ^{181}Ta probe nuclei in GdCoO_3 perovskite at various temperatures. Solid lines are the least squares fit of the theoretical function to the experimental data.

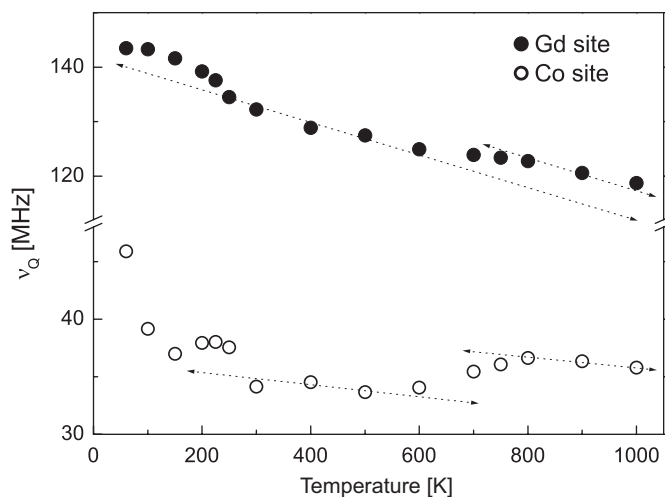


Fig. 3. Temperature dependence of the fitted quadrupole frequencies ν_Q corresponding to ^{111}Cd probes at Gd (full circles) and Co sites (open circles) in GdCoO_3 perovskite.

taken with ^{111}Cd probe at Co sites. For instance, ν_Q is, respectively, for Gd and Co sites, 127(1) and 34.5(3) MHz at 500 K and 122(1) and 36.6(3) MHz at 800 K. Discontinuities at these temperatures have been observed earlier in the magnetic susceptibility data [7] and PAC measurements in LaCoO_3 [2]. These discontinuities were, respectively, 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 HS state ($t_{2g}^4 e_g^2$).

In the case of measurements with ^{181}Ta probe, the temperature dependence of ν_Q shows for both fractions a sudden decrease at temperatures higher than 200 K as shown in Fig. 4. Above this temperature, ν_Q remains almost constant for fraction 2 but, for fraction 1 increases from 400 to 600 K, decreases again up to 850 K and finally shows a small increase at 900 K. The interpretation of this behavior is the following: around 200 K fraction 2 corresponds to Co ions change from LS state directly to HS state and, as fraction 1 decreases from 72% to 20% when temperature increases from 200 to 500 K and increases to 80% at 900 K, we suppose that Co ions for this fraction change to IS state at 200 K and, as temperature increases, change to HS state. This behavior can be ascribed to the doping of the sample with Hf in order to introduce the ^{181}Ta probe, 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.

For both Gd and Co sites except for a small increase in the value in the region from 600 to 800 K, the quadrupole frequencies at ^{111}Cd decrease almost linearly above ~ 200 K with increasing temperature. 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. 3. Since the

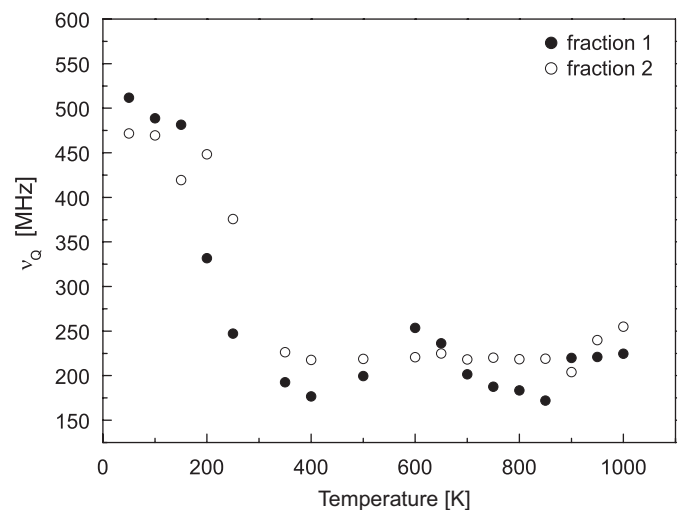


Fig. 4. Temperature dependence of the fitted quadrupole frequencies ν_Q corresponding to two fractions of ^{181}Ta probes at Co sites in GdCoO_3 perovskite.

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, at around 50–75 and 500–600 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 transitions provoke 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.

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