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Investigation of hyperfine interactions in $GdCrO_3$ perovskite oxide using PAC spectroscopy

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Abstract Perturbed angular correlation (PAC) measurements have been carried out in the antiferromagnetic $GdCrO_3$ perovskite oxide using ^{111}In (^{111}Cd) and ^{181}Hf(^{181}Ta) nuclear probes. The radioactive parent nuclei ^{111}In and ^{181}Hf were introduced in the compound through a chemical process during sample preparation. The PAC measurements were carried out in the temperature range 20–300 K. Measurements with the ^{181}Ta indicated a unique quadrupole interaction above 170 K and a combined electric quadrupole and magnetic dipole interactions below this temperature. The observed interaction was assigned to the probe nuclei substituting Cr sites. Measurements with ^{111}Cd showed two quadrupole interactions. Only one of the fractions however, showed a combined electric and magnetic interaction in the temperature rage 20–170 K which was assigned to ^{111}Cd probe substituting Cr site. The other fraction was attributed to the Gd site. The present results are compared with those of $LaCrO_3$ and $NdCrO_3$.

Keywords Gadolinium chromite · Perovskite · Magnetic hyperfine field · PAC spectroscopy

1 Introduction

Perovskite oxides of 3d transition metal, of the type $RCrO_3$, called orthochromites, where R is rare-earth metal are known to exhibit interesting magnetic and structural properties. These perovskites are orthorhombically distorted from the ideal cubic structures at room temperature (space group Pbnm) and usually show temperature dependent structural and magnetic phase transitions. In these compounds, the transition metal Cr as well as the Lanthanides (except La and Lu) may have magnetic moment. The interaction between transition metal and lanthanide ions is quite

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important to determine their magnetic behavior. The compound $GdCrO_3$ has canted-antiferromagnetic order of localized Cr^{3+} spins with a Néel temperature of 170 K [1, 2]. The magnetic properties of Gadolinium orthochromite have been investigated in the past by several techniques [1–4]. However, no microscopic study has been reported. It would therefore be interesting to study $GdCrO_3$ with some microscopic technique and compare the magnetic interactions in this compound, in which the rare-earth metal ion has seven 4f-electrons, with $NdCrO_3$ and $LaCrO_3$ in which there are three and zero 4f-electrons respectively [5, 6]. The present study reports the results of PAC measurements in $GdCrO_3$ using ^{111}In (^{111}Cd) and ^{181}Hf(^{181}Ta) probe nuclei to obtain the temperature dependence of magnetic hyperfine field (mhf) at Cr sites.

2 Experimental procedure

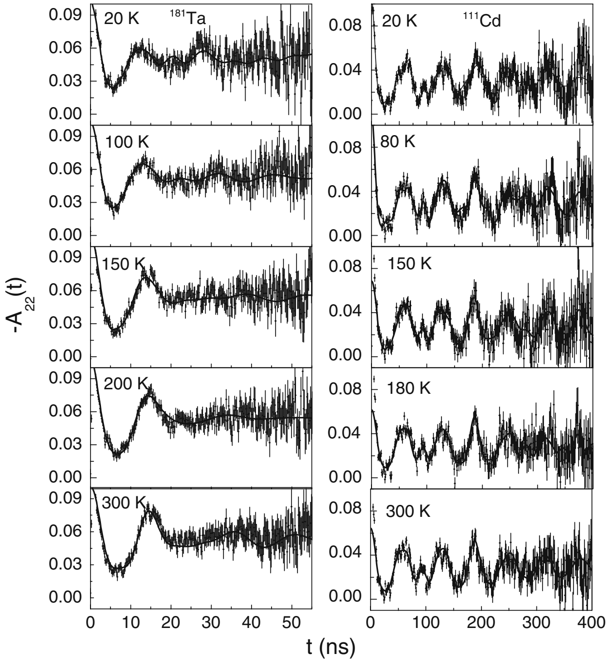
Polycrystalline samples of $GdCrO_3$ were prepared by the citrate sol-gel method starting with high purity Gd (99.99%) and Cr (99.99%) metals. The estoiquiometric quantities of metals were dissolved in nitric acid and hydrochloric acid respectively and the solutions were mixed homogeneously. Known quantities of citric acid and ethylene glycol were added to this solution and the mixture was heated slowly at 100°C for about 10 hours to form the gel. The gel was heated at 500°C for 5 hours to form the oxide powder which was then ground and sintered at 1100°C for about 10 hours. For preparing the samples with radioactive probes approximately 20 μCi of carrier free ^{111}In or ^{181}Hf in the form of dilute solution were added to the mixture of Gd and Cr solutions before the formation of gel. Carrier free ^{111}In in the form of dilute chloride solution was obtained from MS-Nordian. About one milligram of Hf metal was irradiated in the IEA-R1 reactor at IPEN for 10 hours in a flux of 2×10^{13} n cm^{-2} s^{-1} to obtain ^{181}Hf, which was dissolved in HF to obtain a dilute solution. The gel process offers a unique way to introduce the probe ions homogeneously in the sample and this homogeneity is retained even after sintering at high temperature.

The PAC measurements were carried out with a gamma spectrometer consisting of four conical BaF_2 detectors arranged in a planar 90°–180° geometry and an associated slow-fast electronic system for measuring the delayed $\gamma\gamma$-coincidence spectra. The spectrometer records simultaneously 12 delayed coincidence spectra (four spectra with detectors at 180° and 8 with detectors at 90°). Well known gamma cascade of 171–245 KeV in ^{111}Cd populated from the electron capture decay of ^{111}In and 133–482 KeV gamma cascade populated from the β^--decay of ^{181}Hf were used to measure the PAC spectra. Measurements were carried out in the temperature rage of 20–300 K using a closed-cycle helium cryogenic system.

3 Results and discussion

Results of the X-ray diffraction measurement for the sample analyzed by Rietveld method, confirmed a single phase orthorhombic structure with Pbnm space group. Some of the PAC spectra for the $GdCrO_3$ sample measured with ^{181}Hf(^{181}Ta) and ^{111}In (^{111}Cd) probes at selected temperatures are shown in Fig. 1. The spectra above the Néel temperature $T_N = 170$ K were fitted with a model including only the

Fig. 1 PAC spectra for $GdCrO_3$ perovskite measured by ^{181}Ta and ^{111}Cd probes at indicated temperatures. *Solid lines* are the least-squares fit of the data to appropriate theoretical perturbation functions



quadrupole interaction [5] in both cases. In order to fit the perturbation functions measured at temperatures below the Néel temperature, we used a model for the combined electric and magnetic interactions in a polycrystalline sample from which the quadrupole frequency ν_Q as well as the Larmor frequency ω_L can be deduced. Details of PAC method as well as data acquisition and analysis of magnetic interaction in a polycrystalline sample are described in references [5].

The PAC results for ^{181}Ta probe show a unique and well defined quadrupole interaction in the temperature range of 170–300 K and a combined quadrupole and magnetic interaction below 170 K. The quadrupole interaction with hyperfine parameters such as quadrupole frequency ν_Q, asymmetry parameter η and frequency distribution δ as well as the hyperfine field $B_{hf}(0)$ are summarized in Table 1. Included in this table are also de data for $LaCrO_3$ and $NdCrO_3$ [6] for the purpose of comparison. These interactions were attributed to ^{181}Ta probe nuclei occupying Cr sites. The assignment is based on the evidence obtained in a previous PAC study of $La(Cr,Fe,Mn)O_3$ perovskites [7, 8]. From the magnetic interactions observed in $La(Cr,Fe)O_3$ it was concluded that the spin density transferred from the nearest Cr^{3+} (Fe^{3+}) ions to rare-earth atom site via oxygen orbital in super exchange interaction is much smaller compared to the Cr or Fe sites. This conclusion was experimentally confirmed [5] from the PAC measurement of mhf at La sites in $La(Cr,Fe)O_3$ using ^{140}Ce probe, where a very small field of ~0.3 T was observed. From the observed much higher values of $B_{hf}(0)$for $(La,Nd)CrO_3$ measured with ^{181}Ta probe (see Table 1) authors concluded that the this probe substitutes Cr site rather than rare-earth sites.

The temperature dependence of mhf at ^{181}Ta in $GdCrO_3$ measured in the present work is shown in Fig. 2. Solid lines in this figure are the Brillouin functions for

Table 1 Experimental values of hyperfine parameters for the $GdCrO_3$ perovskite measured with ^{181}Ta probe nuclei

Perovskite	ν_Q(MHz)	δ (%)	η	T (K)	B_{hf} (0) (Tesla)
$GdCrO_3$	276.8	2.4	0.62	300	1.1 (1)
$NdCrO_3$	178.9	9.8	0.38	295	1.2 (1)
$LaCrO_3$	153.1	7.3	0.73	295	5.5 (1)

Similar results for $NdCrO_3$ and $LaCrO_3$ taken from reference [6] have been included in this table for the purpose of comparison

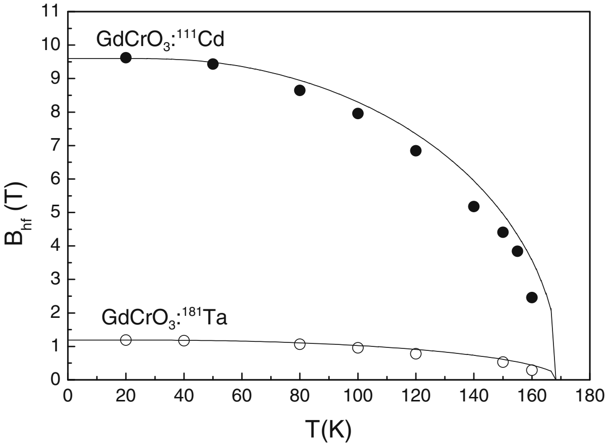


Fig. 2 Temperature dependence of B_{hf} at Cr site in $GdCrO_3$ measured by ^{111}Cd and ^{181}Ta probes. The *solid line* are the Brillouin functions for J = 3/2 corresponding to Cr^{+3} ion

the spin $J = 3/2$ of Cr^{+3} fitted to experimental data. The value of the field $B_{hf}(0)$ extrapolated to 0 K is 1.1(1) T, which is quite similar to that observed for $NdCrO_3$ (see Table 1). We therefore concur with the conclusions drawn from the previous studies and believe that in $GdCrO_3$ also the ^{181}Ta probe substitutes Cr and not Gd sites. As further evidence we cite the results of another study of quadrupole interactions in $LaMnO_3$ measured with ^{181}Ta where it was established that this probe occupies the La site [see reference [7] for details]. As the value of ν_Q observed in $GdCrO_3$ (Table 1) is much smaller than the value of 1000 MHz in $LaMnO_3$we once again conclude that ^{181}Ta probe nuclei substitute Cr rather than Gd.

The PAC measurements in $GdCrO_3$ carried out with ^{111}Cd probe showed two fractions with well defined quadrupole frequencies. The quadrupole frequencies at 300 K are: $\nu_{Q1} = 50.1(4)$ MHz and $\nu_{Q2} = 32.2(4)$ MHz respectively with relative fractions $f_1 = 70\%$ and $f_2 = 30\%$. The quadrupole frequencies decrease slowly and smoothly with increasing temperature. The fraction f_1 decreasesgradually from 70% at 300 K to about 50% at 20 K. The PAC spectra measured below 170 K were analyzed with a model including combined quadrupole and magnetic interactions. While the larger frequency component (f_1) showed a magnetic interaction, there was no indication of magnetic interaction in the f_2 component which showed only pure quadrupole interaction up to the lowest measured temperature. Earlier measurements [5] had shown that ^{111}Cd probe can occupy both transition element as well as rare-earth atom sites. Using similar arguments as given above we assigned the fraction f_1 to ^{111}Cd probe nuclei substituting Cr sites while the other fraction was attributed to Gd site. The mhf at rare-earth atom site is expected to be very much smaller compared to the transition element site from the super exchange interactions with Cr^{+3} ions. The interaction between Gd atoms becomes significant only at a much lower temperature and the ordering of Gd^{+3} moments takes place only at 2.3 K [2]. This is confirmed by the present study as no magnetic interaction was detected at Gd site. The temperature dependence of mhf is shown in Fig. 2 from which the extrapolated value of $B_{hf}(0) = 9.7(1)$ T was derived.

Both ^{181}Ta and ^{111}Cd substitute Cr atoms and they are octahedrally surrounded by six oxygen atoms, which are further bound to six Cr ions as next near neighbors. The hyperfine magnetic field at these probes therefore arises as a result of spin density transfer from Cr ions through Cr–O–Ta(Cd) bonds The transfer takes place through spin polarization of the outer Ta^{+5} (Cd^{+3}) shells by magnetic neighbors through overlap of oxygen p-orbital transferring unpaired spin density in to the outermost Ta(Cd)-orbitals. This interaction is analogous to the indirect Cr–O–Cr exchange interaction and the effective field at ^{181}Ta and ^{111}Cd probes substituting Cr ions is therefore referred as supertransferred magnetic hyperfine field (SMHF).

Gd^{+3} and $Nd+^{3}$ ions have incomplete 4f-shell and in principle should contribute to the hyperfine magnetic field. The observed $B_{hf}(0)$ values for $GdCrO_3$ and $NdCrO_3$ perovskites measured with ^{181}Ta are quite similar but they are much smaller than the corresponding value for $LaCrO_3$ where La^{+3} has no 4f-electrons [5, 6]. The reason for this difference may be understood by considering the local magnetic moments of Cr and rare earth ions both of which contribute to hyperfine fields in these compounds. We may consider the spin-only value for Cr^{+3} ($3d^3$, $\mu_{eff} = 3.87\ \mu_B$) for the purpose of illustration as the orbital contribution is expected to be largely quenched. In the case of $LaCrO_3$ only Cr^{+3} moments contributes to the hyperfine field. However in the case of Nd(Gd)CrO_3 the net effective moment has contributions from Nd^{+3} (Gd^{+3}) moments in addition to Cr^{+3} moment and these must be properly taken in to account. The effective moments in $NdCrO_3$ and $GdCrO_3$ are however considerably reduced in these compounds because Cr^{+3} moment is oriented anti-parallel to those of Nd(Gd) [1, 2] resulting in lower hyperfine fields. It is therefore important to consider the relative importance of Cr–Gd and Cr–Nd interactions in addition to Cr–Cr interactions in determining the hyperfine fields at Cr site in these compounds. The Gd–Gd interactions are important only at very low temperatures.

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