Investigation of hyperfine interactions in RMO_3 (R = La, Nd; M = Cr, Fe) antiferromagnetic perovskite oxides using PAC spectroscopy

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Abstract The local magnetic interaction at the transition metal sites in RMO_3 (R = La, Nd; M = Cr, Fe) compounds has been investigated by perturbed angular correlation (PAC) technique using $^{181}Hf \rightarrow {}^{181}Ta$ probe nuclei. The present measurements cover a temperature range from 10 K to 1000 K. Above the respective Néel temperature, each compound shows a unique quadrupolar frequency that decreases linearly with temperature. These interactions were assigned to the radioactive probe substituting Cr or Fe sites. Below T_N, a combined electric plus magnetic hyperfine interaction was observed. The magnetic interaction revealed that the super transferred hyperfine fields on ^{181}Ta at the Cr sites in $(La,Nd)CrO_3$ extrapolated to 0 K, are much smaller than the corresponding values at Fe sites in $(La,Nd)FeO_3$. This difference was attributed to different distribution of d electrons in Cr^{3+} ($3d^3$) and Fe^{3+} ($3d^5$) ions in each compound. As the fields for Nd compounds are smaller than those for La compounds, the role of rare-earth ions in the magnetism of these oxides is also discussed.

1 Introduction

Perovskite oxides of 3d transition metal of the type RMO_3, where R is a rare-earth element, are known to exhibit interesting transport, magnetic and structural

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properties. In this family, $LaCrO_3$, $LaFeO_3$, $NdCrO_3$ and $NdFeO_3$ order antifer-romagnetically with Néel temperatures of 282, 743, 219 and 687 K respectively. Rare-earth orthochromite $RCrO_3$ and orthoferrite $RFeO_3$ are good candidates for the study of local magnetism, as these perovskites are orthorhombically distorted from their ideal cubic structures and show temperature dependent structural and magnetic phase transitions. In these compounds, Fe and Cr as well as the rare-earth ions (except La and Lu) have magnetic moment and interaction between them is important in determining their magnetic behavior. It would therefore be interesting to compare the local magnetism in compounds with La^{3+}, which have no f electrons, with other rare-earth ion having a few f-electrons, like Nd^{3+}.

The structural and the magnetic phase-transition behavior of the lanthanum and neodymium orthochromite and orthoferrite has been investigated by other techniques, however, only a few microscopic studies on atomic scale have been reported. Recent microscopic investigations of perovskites ABO_3 [1–3] were carried out through determination of the electric field gradient (EFG) and magnetic hyper-fine field (MHF) at probes located on A and B sites, by time differential perturbed angular correlation (TDPAC) technique using ^{111}Cd as probe. In the present work, PAC measurements were performed in $(La,Nd)CrO_3$ and $(La,Nd)FeO_3$ perovskites, at different temperatures, using $^{181}Hf \rightarrow ^{181}Ta$ probe to obtain the temperature dependence of MHF at Cr and Fe sites.

2 Experimental procedure

Polycrystalline samples were prepared by a citrate sol-gel method starting from a mixture of nitrate solutions of the starting materials, La (99.9%) and Nd (99.9%) and Cr (99.99%) and Fe (99.99%), obtained by dissolving the metals in concentrated HNO_3. The radioactive ^{181}Hf was introduced in the samples by adding about 20–30 μCi of ^{181}Hf dissolved in dilute HF to the mixture of nitrate solutions. Approximately 100 mg of each sample, was prepared separately without addition of ^{181}Hf for analysis by the X-ray diffraction method.

The PAC technique was used to measure hyperfine interactions in the polycrys-talline samples using $^{181}Hf \rightarrow ^{181}Ta$ probe nuclei. Details of PAC method as well as data acquisition and analysis of magnetic interaction in a polycrystalline sample are described in references [3] and [4]. The PAC measurements were carried out in the temperature range of 10–1004 K.

3 Results and discussion

The results of the room temperature powder X-ray diffraction measurements for the samples analyzed by the Rietveld method, confirmed a single phase orthorhombic structure in all compounds. The measured crystallographic lattice constants shown in Table 1 are in good agreement with the earlier X-ray measurements. Figure 1a shows PAC spectra for each compound at selected temperatures. The spectra above the respective Néel temperature were fitted by a model including only electric quadrupole interaction [3]. The results show a well-defined quadrupole interaction and an unknown minor fraction (less than 10%) for each sample except for $LaFeO_3$

Table 1 Experimental values of lattice parameters and hyperfine parameters for the studied perovskite compounds

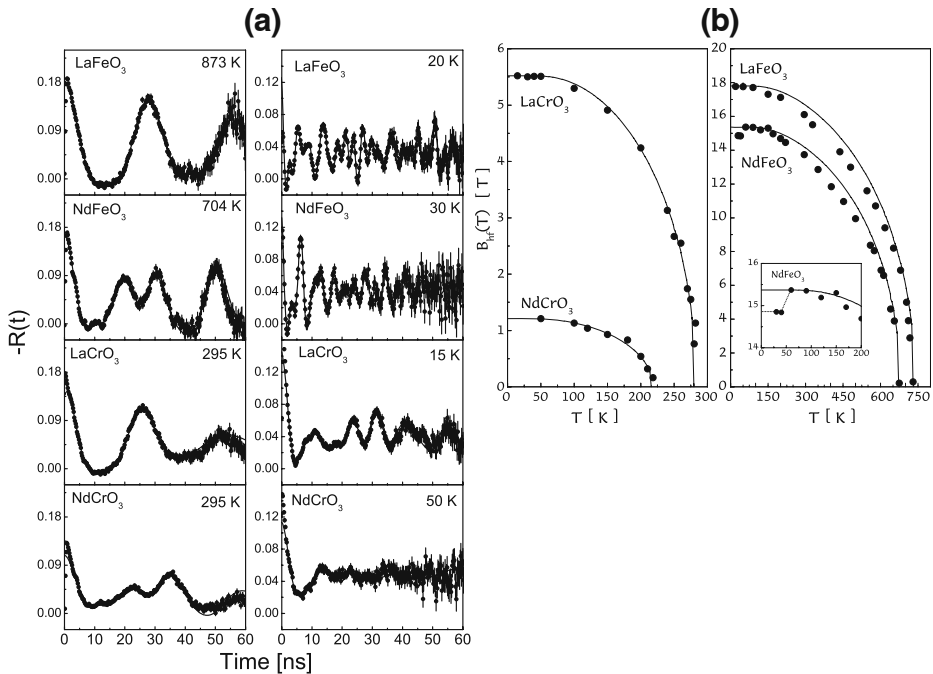| Compound	Lattice parameter[a] (Å)			ν_Q (MHz)	δ (%)	η	T (K)	$B_{hf}(0)$ Tesla
	a	b	c					
$LaCrO_3$	5.479(5)	7.759(7)	5.513(6)	153.1	7.3	0.728	295	5.5(1)
$LaFeO_3$	5.553(5)	7.857(7)	5.563(6)	137.4	3.3	0.823	873	17.8(1)
$NdCrO_3$	5.422(5)	7.692(7)	5.484(6)	178.9	9.8	0.380	295	1.2(1)
$NdFeO_3$	5.451(5)	7.762(7)	5.586(6)	216.2	5.0	0.569	704	15.4(1)

[a] measured at room temperature

where a unique interaction was observed. The observed minor fractions do not show significant temperature dependence and their origin is not well understood.

The major quadrupole interaction with respective hyperfine parameters as well as the magnetic hyperfine fields obtained at the indicated temperatures are summarized in Table 1. These interactions were assigned to ^{181}Ta probe nuclei occupying Cr(Fe) sites. The assignments are based on evidence obtained from previous PAC studies of $LaCrO_3$ and $LaFeO_3$ and $LaMnO_3$ [5, 6]. From the results of magnetic interactions in $LaCrO_3$, $LaFeO_3$ it was concluded that the spin density transferred from the nearest $Cr^{3+}(Fe^{3+})$ions to rare-earth sites in super exchange interaction should be much smaller than to Cr or Fe sites. The confirmation came from the PAC measurements of MHF at La sites in $LaCrO_3$ and $LaFeO_3$ using ^{140}Ce probe where only a small field ($\sim$0.3 T was obtained for both compounds) [3]. As the B_{hf} values observed in (La,Nd)CrO_3 and (La,Nd)FeO_3 are considerably larger we conclude that ^{181}Ta occupies Cr and Fe sites rather than La and Nd sites. On the other hand results of quadrupole interactions in $LaMnO_3$ established that ^{181}Ta occupies La site in this compound(for details see [5]. As the values of ν_Q observed in (La,Nd)CrO_3 and (La,Nd)FeO_3 are much smaller than the value of 1,000 MHz for $LaMnO_3$ we once again conclude that the probe nuclei ^{181}Ta occupies Cr(Fe) sites and not rare earth site.

As Ta^{5+} probes substitute the transition metal ions Cr^{3+} or Fe^{3+}, they are octahedrally surrounded by six oxygen ions, which are further bound to six transition metal ions all belonging to the same sub-lattice. Therefore, a hyperfine magnetic field at the ^{181}Ta arises as a result of spin density transferred from $Cr^{3+}(Fe^{3+})$ ions through $Cr^{3+}(Fe^{3+})$-O^{2-}-Ta^{5+} bonds. The transfer occurs through the spin polarization of the outer Ta^{5+}-shells by magnetic neighbors through the overlap of the oxygen p-orbital transferring unpaired spin density into the outermost Ta-orbital. The effective field at Ta^{5+} is therefore referred to as the supertransferred magnetic hyperfine field (SMHF).

Below their respective magnetic transition temperatures, PAC spectra show well defined combined electric quadrupole plus magnetic dipole interactions, from which the magnetic hyperfine fields can easily be deduced. The spectra of $NdCrO_3$ show a damping below 210 K that continues up to 50 K. The temperature dependence of the magnetic hyperfine fields (B_{hf}) are shown in Fig. 1b.

The solid lines in the Fig. 1b show the Brillouin function for the J-spin of Cr^{3+} or Fe^{3+} fitted to the experimental data yielding $B_{hf}(0)$values which are shown in Table 1. The values at Cr sites in both compounds are much smaller than the values for Fe site. The same behavior was observed for MHF at ^{111}Cd in $LaCrO_3$ and $LaFeO_3$ in a previous work [3]. The explanation for this lies in the fact that orbitals

Fig. 1 **a** PAC spectra for studied perovskites measured with ^{181}Ta at indicated temperatures. *Solid lines* are least-squares fits of the theoretical perturbation functions to the experimental data. **b** Temperature dependence of B_{hf} at M sites in $(La,Nd)CrO_3$ and $(La,Nd)FeO_3$ perovskites measured with ^{181}Ta. The *solid lines* represent the Brillouin function for $J = 3/2$ corresponding to the $Cr(Fe)^{3+}$ ion. The behaviour of B_{hf} in $NdFeO_3$ at lower temperature is better seen in the *inset*. The *dotted line* in the inset is only a visual guide

with rotational symmetry around the bond axis like e_g orbitals in $Cr^{3+}(Fe^{3+})$ or p-orbitals of O^{2-} transfer maximum spin density to the orbitals in Ta^{5+}. In Cr^{3+} ($t_{2g}^{3\uparrow}e_g^0$) the e_g orbitals are empty and the t_{2g} orbitals, which have relatively small overlap with the orbitals of nearby oxygen or rare earth ions, tend to form a localized t_{2g} ion core and transfer less spin density to Ta^{5+} orbitals via Cr^{3+}-O^{2-}-Ta^{5+} exchange bonds in $RCrO_3$ compared to $RFeO_3$ since e_g orbitals in Fe^{3+} ($t_{2g}^{3\uparrow}e_g^{2\uparrow}$) have two spin-up electrons. Another reason that makes B_{hf} smaller in $RCrO_3$ than in $RFeO_3$ is the polarization of p-orbitals of oxygen as a result of charge transfer to unoccupied d-orbitals of Cr^{3+}. Due to the strong intra-atomic interaction with the localized t_{2g} spin-up electrons, the transfer of oxygen p-electrons with spin-up into the empty e_g orbital of Cr^{3+} predominates resulting in a negative spin density of oxygen p-orbitals. As a consequence, much less spin density is transferred to Ta^{5+} ion in $RCrO_3$ than in $RFeO_3$ where the d-orbitals of Fe^{+3} (t_{2g} and e_g) are half filled.

Although Nd^{3+} ions have incomplete $4f$ shell, the $B_{hf}(0)$ values for Nd compounds are smaller than for the corresponding La compounds. The reason for this difference may be understood from the consideration of local magnetic moments, which are the principal source of hyperfine field in these oxides. Whereas in $LaFe(Cr)O_3$ only Fe(Cr) atoms contribute to the total magnetic moment with values

of μ_{Fe} 4.6(2) μ_B and μ_{Cr} = 2.8(2) μ_B respectively [7] for NdFe(Cr)O$_3$ the net magnetic moment has contributions from Fe(Cr)as well as from Nd atoms. In NdFeO$_3$ although the values of Fe and Nd moments are μ_{Fe} = 3.97(5) μ_B and μ_{Nd} =1.10(7) μ_B respectively [8] effective moment comes only from Fe atom since Nd moments are oriented perpendicular to the Fe moments. On the other hand in the case of NdCrO$_3$ the net moment is considerably reduced as the Cr moment (μ_{Cr} = 2.52(20) μ_B) and Nd moment(μ_{Nd} = 1.93(30) μ_B) are oriented anti-parallel to each other [9]. The role of Nd-Fe and Nd-Cr magnetic interactions therefore seem to play an important role in determining the observed hyperfine fields in NdFe(Cr)O$_3$ oxides [10].

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