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Study of the local magnetic environment in $LaMnO_3$ perovskite by measuring hyperfine interactions

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Abstract

TDPAC technique has been used to investigate the hyperfine interactions in the $LaMnO_3$ perovskite using $^{140}La(^{140}Ce)$ as probe nuclei. Temperature dependence of the magnetic hyperfine field (MHF) at La sites shows an antiferromagnetic behavior with Néel temperature around 142 K. For temperatures below 80 K, however, the values of MHF decrease and deviate from the expected regular behavior.

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Perovskite oxides of the type $LaMO_3$ where M is a 3d transition metal such as Cr, Fe, Co or Mn exhibit a variety of unusual and interesting transport, magnetic and structural properties. The most studied, among these, in the last decade is Lanthanum manganite ($LaMnO_3$), which exhibits the colossal magnetoresistance and a complex magnetic behavior. The stoichiometric compound with only Mn^{3+} ion is a semiconductor at room temperature, and an antiferromagnet with the Néel temperature $T_N = 140$ K [1]. The replacement of La with alkaline-earth atoms as well as an excess of oxygen in the sample (e.g. $LaMnO_{3+\delta}$, $\delta > 0$) induces the co-existence of Mn^{3+} and Mn^{4+} ions.

Although it would be interesting to investigate many of the properties of the $LaMO_3$ perovskites from a microscopic point of view, only few studies on atomic scale have been reported. Recent microscopic investigations of perovskites of the type ABO_3 were carried out by measuring the electric field gradient (EFG) and magnetic hyperfine field (MHF) at nuclear probes located at both A and B sites using time differential perturbed angular correlation (TDPAC) spectroscopy [2–4]. This method offers a high sensitivity to local crystallographic variations and charge distributions around the lattice site substituted by the probes and consequently can be used to detect changes such as bond distances, symmetry, defect trapping etc. through MHF or EFG measurements to investigate distinct microscopic processes in these materials. Previous TDPAC investigations [5,6] of $LaMnO_3$ using ^{181}Ta claimed that the probe nuclei substituted the Mn atom sites. The authors argued that the expected MHF at the La site would be very small or even vanish, while the probe at Mn site would show a stronger magnetic interaction. In order to further explore this fact we have used, in the present work, a different probe nuclei, $^{140}La(^{140}Ce)$ to investigate the MHF at the La site.

A wet chemical route was used to prepare the polycrystalline samples of $LaMnO_3$. Stoichiometric quantities of La_2O_3 (99.9%) and metallic Mn (99.9%) were dissolved separately in concentrated HNO_3 to obtain the nitrate solutions. To reduce the higher valence manganese ions, a few crystals of hydroxylamine hydrochloride were added to the $Mn(NO_3)_3$ solution.

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The two solutions were mixed together and slowly evaporated to dryness. The resulting powder was further heated at 600°C in air, pressed into a pelett and sintered at 1300°C in air for 24 h. The pelett was cooled to room temperature and then heated in vacuum at 1300°C for 3 days. Approximately 100 mg of the sample was irradiated with neutrons in the nuclear reactor at IPEN to produce ^{140}La activity. TDPAC measurements were carried out in the temperature range of 10–140 K, using 329–487 keV gamma cascade in the decay of $^{140}\text{La} \rightarrow {}^{140}\text{Ce}$ to investigate the temperature dependence of MHF at the La site.

The TDPAC technique is based on the hyperfine interaction of the nuclear moments of the probe nuclei and the extra nuclear magnetic field or electric field gradient. Since the electric quadrupole moment of the intermediate level of the ^{140}Ce probe is very small, one expects an almost pure magnetic dipole interaction at the La site. The experimental data were fitted using the standard model for magnetic interactions. Further details about the TDPAC technique and the experimental procedure are described in Ref. [4]. The fitting of the spectrum at 90 K, for instance, resulted in a major component ($f \sim 70\%$) with a Larmor frequency $\omega_L = 223.8(1)$ Mrad/s corresponding to the magnetic field $B = 4.2(1)$ T. The origin of the second minor component was not determined, but it could be related to the presence of different La sites in the lattice due to structural defects or oxygen vacancies observed in the quadrupole interaction measurements with the other probes.

The ^{181}Hf(^{181}Ta) probe was previously reported [6] to replace Mn atoms in $LaMnO_3$. It was based on the perception that the transfer of spin density in the perovskite structure from one cation site to any other, via the oxygen p-orbital, is only favorable when the metal–ion–oxygen–metal-ion bond angle approaches 180°. Catchen et al. determined the extrapolated value of the MHF at 0 K to be 3.48 T and argued that this relatively high value would be observed only if the ^{181}Ta probe was at Mn site were the Mn–O–Mn angle is close to 180°. They disregard the possibility of the probe occupying the La position, since the La–O–La angle is around 90° and consequently should have very small MHF. In the present work we have used ^{140}La(^{140}Ce) probe to measure the MHF at La site and obtained a value, extrapolated to 0 K, of 5.4 T, which is of the same order of magnitude as the value measured with ^{181}Ta. There is no doubt about the location of ^{140}Ce probes because they are the product of the radioactive decay of ^{140}La nuclei produced in $LaMnO_3$ samples by neutron irradiation. The MHF at La sites in the analogous compounds $LaCrO_3$ and $LaFeO_3$ using ^{140}La(^{140}Ce) probes was found to be much smaller, of the order of 0.3–0.4 T in comparison with the values of 2.5 and 19.4 T obtained for ^{111}Cd probe at Cr and Fe sites, respectively [4]. One should, therefore, expect a much higher value of MHF at ^{181}Ta on Mn sites in $LaMnO_3$ compared to La sites despite the characteristic differences between the probes utilized. Additional evidence is obtained from the NMR measurement of the local field in $LaMnO_{3+\delta}$ using ^{139}La. The reported value [7] for $\delta < 0.1$ of ~ 3 T is of the same order of magnitude as our result. We therefore conclude that the ^{181}Ta probe in the earlier measurements was indeed located at La rather than on Mn sites.

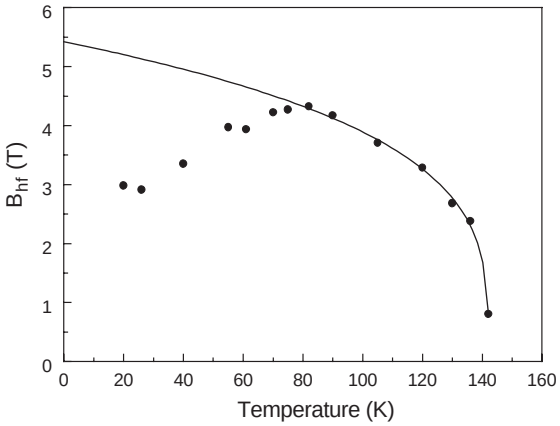

Fig. 1. The temperature dependence of the magnetic hyperfine fields at the La site below T_N.

The temperature behavior of the magnetic hyperfine field is presented in Fig. 1. Using the data corresponding to the five temperature values immediately below the critical temperature T_N, we could fit the well-known power law $B(T) = B(0)(1 - T/T_N)^{\beta}$ expected for magnetic materials where $B(0)$ is the MHF at 0 K and β is the critical exponent near the critical temperature. The result of the fitting, which is shown as a solid curve in Fig. 1, yielded $B(0) = 5.4(2)$ T, $T_N = 142.1(2)$ and $\beta = 0.27(2)$. The value of the critical exponent agrees quite well with $\beta = 0.28$ obtained by neutron scattering measurements [7].

The MHF values follow the fitted curve for temperatures higher than 80 K, but for lower temperatures the MHF sharply decreases, departing from the expected curve. This behavior is not understood, but could be related to the nature of the ^{140}Ce probe, which has one 4f electron that can be polarized and affect the MHF.

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