

A ^{55}Mn NMR Study of $\text{La}_{0.33}\text{Nd}_{0.33}\text{Ca}_{0.34}\text{MnO}_3$ with ^{16}O and ^{18}O

D. RYBICKI^a, CZ. KAPUSTA^a, P.C. RIEDI^b, C.J. OATES^a,
M. SIKORA^a, D. ZAJĄC^a, J.M. DE TERESA^c, C. MARQUINA^c
AND M.R. IBARRA^c

^aDepartment of Solid State Physics, Faculty of Physics and Nuclear Techniques
AGH University of Science and Technology
Al. Mickiewicza 30, 30-059 Cracow, Poland

^bDepartment of Physics and Astronomy, University of St. Andrews
St. Andrews, KY16 9SS, Scotland, United Kingdom

^c Instituto de Ciencias de Materiales de Aragon, Universidad de Zaragoza CSIC
50009 Zaragoza, Spain

A ^{55}Mn NMR study of ^{16}O and ^{18}O containing $\text{La}_{0.33}\text{Nd}_{0.33}\text{Ca}_{0.34}\text{MnO}_3$ is reported. The spin-echo spectra measured at 4.2 K and zero field consist of a double exchange line corresponding to the ferromagnetic metallic regions. The line intensity is more than an order of magnitude lower for the ^{18}O compound, which indicates an order of magnitude lower content of the ferromagnetic metallic phase in this compound. The frequency dependence of the spin-spin relaxation time T_2 shows a pronounced minimum at the center of the double exchange line of both compounds due to the Suhl-Nakamura interaction, which indicates that the ferromagnetic metallic regions are at least 10 nm in size. The results are discussed in terms of the influence of oxygen isotopic substitution on phase segregation.

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1. Introduction

Manganese perovskites are of considerable interest owing to their magnetoresistive properties which make them promising candidates for applications in spin electronics and data storage technology. They also exhibit a variety of different

electronic and magnetic phases due to the strong competition between double exchange (DE), superexchange (SE) and electron–phonon interactions. Such interactions can be easily influenced by chemical substitution, external pressure, magnetic field and isotopic exchange, which in manganese perovskites were first studied in the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+y}$ compounds [1]. Also in the $(\text{La}_{1-x}\text{Nd}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ series the magnetic behavior is tremendously sensitive to alkaline earth doping. For $x < 0.5$, there are para-ferromagnetic and metal–insulator transitions, whereas for $x > 0.5$ there is no metal–insulator transition and for $x = 1$, the sample is characterized as charge ordered (CO) [2]. Raman scattering studies in ^{16}O compound showed the coexistence of the ferromagnetic (FM) and CO phases below 100 K and below 50 K in the ^{18}O sample [3].

The crystallographic structure of the compounds studied in the present work belongs to the $Pbnm$ space group. The ^{16}O sample, which contains oxygen of the natural isotopic abundance, i.e. 99.76% ^{16}O , was prepared by conventional solid state reaction using La_2O_3 , Nd_2O_3 , CaCO_3 , and MnO_2 . The powders were mixed, ground, and calcined in air at 1100°C for 15 h. Afterwards, the samples were reground thoroughly, pressed, and fired at 1250°C for 60 h with two intermediate grindings. The oxygen isotope substitution was carried out by a 48 h annealing at 950°C and ^{18}O pressure of 1 bar. The sample showed $80 \pm 10\%$ of ^{18}O [4]. Ibarra et al. [4] studied the isotopic effect in these systems: both compounds, ^{16}O and ^{18}O containing, segregate into a CO paramagnetic phase and a ferromagnetic metallic phase below 210 K and the relative percentage of both phases depends on the isotope mass. At low temperatures the CO phase orders antiferromagnetically (AFM), whereas the remaining phase orders ferromagnetically.

The electrical resistivity at low temperatures is two orders of magnitude smaller than at 200 K for ^{16}O containing compound [5]. Replacing ^{16}O with ^{18}O increases the resistivity by five orders of magnitude at 70 K [4]. The measurements of the volume thermal expansion of the compounds show that the ^{16}O containing sample reaches a complete metallic state at 30 kOe. For the ^{18}O containing sample its ground state is not fully metallic, but phase segregated at 30 kOe. Application of a magnetic field as high as 60 kOe to the ^{18}O containing sample leads to a complete metallic state at low temperatures.

Neutron diffraction measurements carried out at different temperatures showed the presence of a ferromagnetic phase below 200 K and a long-range AFM order within the CO region below 170 K. The results suggested that a strong electron–phonon interaction, which leads to charge localization, plays an important role in weakening the ferromagnetic interaction. This may cause a blocking of electron (hole) hopping between the Mn cations and lead to the localization of charge carriers. It was theoretically predicted that replacing ^{16}O with ^{18}O decreases the Mn–O bond length by about 0.025% at 0 K, which can significantly influence physical properties of the material [6]. A possible inaccuracy of the determination of the oxygen isotopic abundance has also to be accounted for [7].

2. Results

This article presents a ^{55}Mn NMR study of the effect of oxygen isotopic substitution in $(\text{La}_{0.5}\text{Nd}_{0.5})_{0.66}\text{Ca}_{0.34}\text{MnO}_3$. The NMR measurements were carried out with a spin-echo technique [8] at zero field and at 4.2 K. The NMR signal occurs when the resonance condition is met; that is, $2\pi\nu = \gamma|B_e|$, where ν is the resonant frequency and γ is the nuclear gyromagnetic ratio of the isotope. B_e is the internal effective field at the nucleus, which is predominantly of hyperfine origin and is known as the hyperfine field (HFF).

Figures 1 and 2 present NMR spectra of ^{16}O and ^{18}O containing compounds, respectively. The spectra taken at a small pulse separation exhibit a single line, which, similarly to a metallic $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [9], is attributed to the DE driven hopping of electron (hole) between adjacent Mn^{3+} and Mn^{4+} sites via oxygen antibonding orbitals. This particular electron (hole) hopping leads to ferromagnetic coupling of manganese ions of different nominal valency and gives rise to metallic behavior. This is the clear evidence of the presence of ferromagnetic metallic regions in the compounds. The existence of a single line indicates that the characteristic time of electron (hole) hopping is much smaller than the period of the Larmor precession of ^{55}Mn nuclear spins (characteristic time for DE is found to be smaller than 10 ps). For both compounds the hyperfine fields, B_e , were obtained. They amount to -36.24 T for ^{16}O containing sample and -36.26 T for ^{18}O substituted compound.

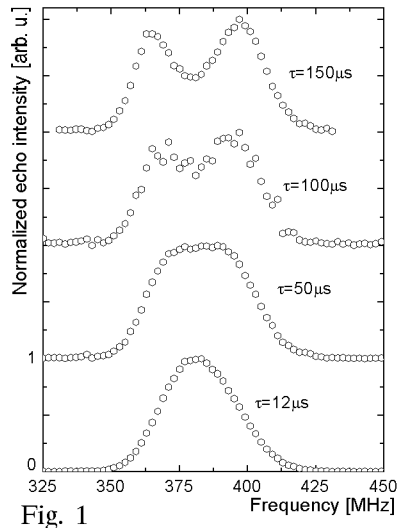


Fig. 1

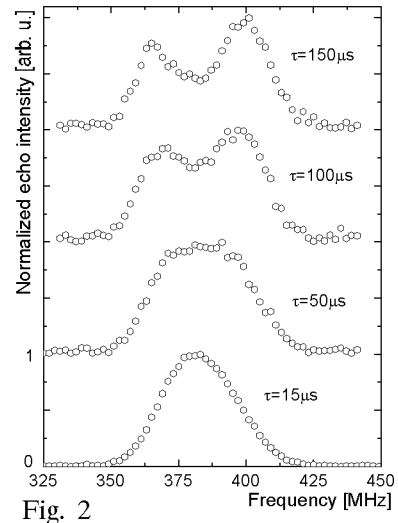


Fig. 2

Fig. 1. ^{55}Mn NMR spin-echo spectra of ^{16}O containing $\text{La}_{0.33}\text{Nd}_{0.33}\text{Ca}_{0.34}\text{MnO}_3$ at 4.2 K for different pulse spacing τ .

Fig. 2. ^{55}Mn NMR spin-echo spectra of ^{18}O containing $\text{La}_{0.33}\text{Nd}_{0.33}\text{Ca}_{0.34}\text{MnO}_3$ at 4.2 K for different pulse spacing τ .

As the pulse separation increases, a dip at the center of the resonance line appears. This feature is also observed in the ^{55}Mn spectra of metallic ferromagnetic manganites [10], and is attributed to the Suhl–Nakamura interaction [11, 12] between neighboring nuclear spins. This interaction originates from an indirect spin–spin coupling mediated by virtual spin waves. The nuclear spin, which sees the electronic spin on its own ion through the hyperfine coupling, excites a spin wave through this coupling, and another nuclear spin causes it to be reabsorbed through its hyperfine coupling [12]. The observed dependence of the spectra on the pulse separation means that nuclear spins, which precess at or near the central frequency, reveal a faster spin–spin relaxation than spins contributing to the wings of the resonance line. As the center of the DE resonance line originates mainly from the spins inside the DE regions, a minimum at the line center denotes that the neighboring manganese ions are magnetically equivalent which makes the Suhl–Nakamura interaction effective. It is much less effective at the boundaries of DE regions where manganese neighbors differ in terms of magnetic moment values and directions, which prevent the exchange of virtual spin waves and results in a slower spin–spin relaxation. Following the evaluation of the effective range of the Suhl–Nakamura interaction presented in [10] we can conclude that the DE regions in our compounds have their average size comparable or larger than 10 nm.

Optimal pulse lengths for both samples are of the same value which means that the NMR enhancement factor, η , is the same in both compounds. This is another proof that the size of the ferromagnetic regions is comparable in both compounds. Thus, at the same mass of the samples, the signal intensity can be considered as a measure of the ferromagnetic metallic (FMM) phase content. The absolute intensity of the DE line in the ^{16}O containing $\text{La}_{0.33}\text{Nd}_{0.33}\text{Ca}_{0.34}\text{MnO}_3$ is twenty times larger than that of the ^{18}O containing compound (Fig. 3). This indicates that the content of the FMM phase in the ^{16}O containing compound is an order of magnitude higher than in the ^{18}O containing compound. There is no

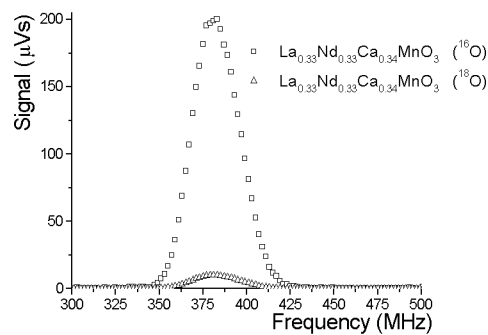


Fig. 3. Comparison of absolute intensities of the ^{55}Mn NMR spectra for the ^{16}O and ^{18}O containing $\text{La}_{0.33}\text{Nd}_{0.33}\text{Ca}_{0.34}\text{MnO}_3$ compounds at 4.2 K and pulse spacing $\tau = 15 \mu\text{s}$.

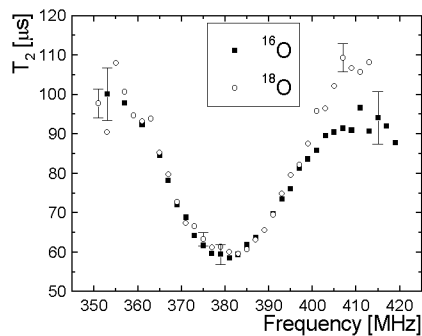


Fig. 4. Frequency dependence of the spin–spin relaxation time, T_2 , at 4.2 K for compounds with different oxygen isotope content.

clear evidence of a signal from the CO insulating AFM phase in the ^{55}Mn spectra, which may be due to a fast nuclear spin–spin relaxation in such a phase.

Figure 4 shows the frequency dependence of ^{55}Mn spin–spin relaxation time, T_2 , for the compounds with different oxygen isotope substitution. One can see a characteristic minimum of T_2 at the frequency corresponding to the center of the resonant line. The plot illustrates quantitatively the contribution of the Suhl–Nakamura interaction to the spin–spin relaxation. Similar values and frequency dependences of T_2 for both compounds (e.g. for $f = 381$ MHz, T_2 is $58 \mu\text{s}$ and $60 \mu\text{s}$ for ^{16}O and ^{18}O containing compounds, respectively) also suggests that the size of FMM regions in both samples is comparable and/or much larger than the Suhl–Nakamura interaction length.

3. Conclusions

Summarizing, our results show that the ^{55}Mn NMR spectra of ^{16}O and ^{18}O containing $\text{La}_{0.33}\text{Nd}_{0.33}\text{Ca}_{0.34}\text{MnO}_3$ compounds exhibit a DE line which corresponds to the existence of FMM regions in both compounds. The spectra and the frequency dependence of T_2 reveal the effect of the Suhl–Nakamura interaction and allow the estimation of the minimum size of the DE regions at 10 nm for both compounds. A much larger absolute intensity of the NMR signal in the ^{16}O containing compound indicates that the contribution of the DE phase is an order of magnitude larger than in the ^{18}O containing compound. The results show that oxygen isotopic substitution influences the phase segregation at low temperatures by decreasing considerably the relative amount of the FMM phase upon ^{16}O substitution by ^{18}O .

Acknowledgments

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