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ABSTRACT
Recently, we had reported the detection of electron paramagnetic resonance (EPR) from magnetoimpedance (MI) measurements in bulk La$_{0.40}$Ca$_{0.60}$MnO$_3$ (LCMO) samples using radio frequency (rf) currents [U. Chaudhuri and R. Mahendiran, Appl. Phys. Lett. 115, 092405 (2019)]. Here, we report an alternative method which involves measuring the effective MI changes of a copper stripcoil that encloses the LCMO sample. Magnetoresistance ($\Delta R/R_0$) and magnetoreactance ($\Delta X/X_0$) of the sample were measured indirectly via the stripcoil for frequencies of current $f = 0.5$ to 2.5 GHz. During the field sweep, $\Delta R/R_0$ shows an abrupt increase that is accompanied by a dip in $\Delta X/X_0$ at a critical value of dc magnetic field ($H_c$) when $f \geq 0.9$ GHz. $H_c$ increased linearly with frequency ($f$) of the current in the stripcoil, satisfying the EPR relation $f_c = (\gamma/2\pi)H_0$, where $\gamma$ is the gyromagnetic ratio and $f_c$ is the resonance frequency. The same stripcoil and the sample were also used to measure microwave power absorption using a vector network analyzer. The features observed in both these techniques were strikingly similar to the results obtained from the direct MI measurement in LCMO, which confirms the electrical detection of EPR.

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Electron paramagnetic resonance (EPR) is a powerful technique to detect unpaired electrons and their interactions with environment in solids. Conventionally, EPR measurement is performed using the microwave cavity resonance method in which a sample placed inside a resonant cavity is irradiated with microwaves of a fixed frequency ($f \sim 9.8$ GHz), and sweeping an external dc magnetic field causes maximum absorption of microwave energy when the resonance condition is satisfied. On the other hand, some studies have shown the possibility of detecting EPR, ferromagnetic resonance (FMR), and nuclear magnetic resonance (NMR) via changes in the photocurrent or dc voltage signals rather than power absorption in a sample exposed to a microwave electromagnetic field. Recently, our group has shown that one can observe EPR features in a bulk sample of the La$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.35$–$0.60$) series via the magnetoimpedance (MI) method which involves measuring the radio-frequency (rf) electrical impedance ($Z = R + iX$, where $R$ is the ac resistance and $X$ is the reactance) of these samples during magnetic field sweep by an rf impedance analyzer. The flow of rf current in the sample induces a circumferential magnetic field in the sample. This rf field ($H_{rf}$), when perpendicular to the applied dc magnetic field, excites Zeeman transitions in Mn$^{3+}$ and Mn$^{4+}$ ions as the dc magnetic field ($H_0$) is swept. rf magnetoresistance (MR) and magnetoreactance (MX) display characteristic features at a critical field value which followed EPR relations. However, high-frequency impedance of a conducting sample in a strong skin depth regime is dependent both on the resistivity and the magnetic permeability of the sample ($Z = \sqrt{-i2\pi f\mu_0\mu\rho}$), where $\mu$ is the dynamic permeability, $\mu_0$ is the vacuum permeability, $\rho$ is the dc resistivity, and $f$ is the frequency of the rf current. Thus, a fundamental question arises as to whether the observed features in the MI measurements observed in Ref. 7 are predominantly affected by the changes in the dynamic permeability ($\mu$) or due to mechanisms related to electrical dc resistivity (or conductivity). Electrical conduction in the paramagnetic state of manganites is due to hopping of $e_g$ electrons ($S = 1/2$) between Mn$^{3+}$ and Mn$^{4+}$ ions in the background of immobile $t_{2g}$ core spins ($S = 3/2$). Strong Hund’s coupling between mobile and core electron spins ensures that the $e_g$ spin is parallel to $t_{2g}$ core spins. When the core spin oscillates in response to $h_{rf}$ generated by the rf current in the sample, it can affect the scattering probability of the $e_g$ electron and, hence, the resistance. Thus, it is necessary to investigate
MI via indirect methods, as employed in this article, to understand the mechanisms behind the high frequency MI in manganites.

We synthesized a polycrystalline La$_{0.6}$Ca$_{0.4}$MnO$_3$ (LCMO) sample by the standard solid state reaction method and characterized the sample by room temperature X-ray diffraction and by using the temperature and field dependence of magnetization (M) measurements. The ferromagnetic Curie temperature ($T_C$) of the LCMO sample was 267 K. A sample of size 7 mm was prepared by the standard solid state reaction method and characterized by room temperature X-ray diffraction and by using the temperature and field dependence of magnetization (M) measurements. The ferromagnetic Curie temperature ($T_C$) of the LCMO sample was 267 K.

A sample of size 7 mm was cut from a pellet and inserted into a cuboidal copper stripcoil of similar dimensions made from 0.2 mm thick copper sheet, as shown in Figs. 1(a) and 1(b). The stripcoil method was previously used by us to investigate high frequency magnetization dynamics in the Co$_{0.7}$Zn$_{0.3}$Fe$_{1.7}$Mn$_{0.3}$O$_4$ bulk sample. One end of the stripcoil was connected to the signal line, and the other end was soldered to the ground of a Sub Miniature version A (SMA) connector. A semirigid $rf$ coaxial cable was used to connect the SMA connector to an $rf$ impedance analyzer (Agilent model E4991A) or a vector network analyzer (VNA) (Agilent model E4991A) or a vector network analyzer (VNA) (Agilent model E4991A) or a vector network analyzer (VNA) (Agilent model E4991A). The stripcoil with the sample was placed at the center of the poles of an electromagnet, creating an axial magnetic field inside the stripcoil, as shown in Fig. 1(b). The stripcoil with the sample was placed at the center of the poles of an electromagnet, and the $R$ and $X$ components of impedance were measured by the impedance analyzer while varying $H_{dc}$ for different frequencies of $rf$ current.

MR and MX were calculated using the standard definitions: $MR(\%) = [R(H_{dc}, f) - R(0, f)]/R(0, f) \times 100$ and $MX(\%) = [X(H_{dc}, f) - X(0, f)]/X(0, f) \times 100$, where $R(H_{dc}, f)$ and $X(H_{dc}, f)$ are the resistance and reactance at a particular frequency ($f$) of $rf$ current and $H_{dc}$, respectively. At resonance, maximum power is absorbed by the sample from the electromagnetic wave. This absorbed power was also detected by measuring the magnetic field dependence of $rf$ power absorption using the VNA over a broad frequency range (10 MHz–2.5 GHz). The reflection coefficient, $S_{11}$, was measured by the VNA, and the power absorbed by the sample was determined by subtracting the contribution of the empty coil from $S_{11}$ values measured with the sample: $ΔP(H) = S_{11}^{\text{sample}}(H) - S_{11}^{\text{empty}}(H)$. This was incorporated to verify whether the observed MR and MX features corresponded to a resonance feature. All the measurements were recorded at room temperature since our experimental setups are currently suitable for room temperature measurements only.

The $ac$ MR and $–MX$, as measured by the stripcoil, are displayed in Figs. 2(a) and 2(b), respectively, as a function of $f$ and $H_{dc}$. The $ac$ MR is negative in the entire field range for $f < 900$ MHz, whereas the $ac$ MR for $f ≥ 900$ MHz increases slowly as the magnetic field increases from the zero value and then shows an abrupt increase at a critical value of the magnetic field ($H_c$). Hence, the sign of the $ac$ MR changes from negative to positive at $H_c$. On the other hand, the field dependence of $–MX$ shows a dip around 0 Oe field for $f < 800$ MHz but shows two symmetrical peaks about the origin for $f ≥ 800$ MHz. In the experiment, MX displays a dip, but we have presented as $–MX$, as shown in Fig. 2(b), for clarity. These features were similar to the direct MI measurements reported earlier in Ref. 7, barring variations in magnitude. In Fig. 2(c), the change in power absorption ($−ΔP$) as measured by the VNA is also shown for different frequencies of the $rf$ signal while varying the $dc$ magnetic field. $ΔP$ is shown with a negative sign, which indicates that the power was absorbed as the magnetic field was increased. Similar
to the ac MR in the strip coil measurement, $-\Delta P$ shows symmetrical features about the origin at $\pm H_r$ and the line shapes are strikingly similar to the ac MR line shapes. The sourced rf power (1 dBm for the impedance analyzer and 10 dBm for the VNA) is absorbed at a sample from the rf magnetic field is related to the imaginary part of the permeability, $\mu''$, according to the relation $P_{\text{ac}} = \frac{1}{2} V_0^2 \omega \mu''$, where $\omega = 2 \pi f$, $f$ is the frequency of current, and $V$ is the sample volume. The characteristic double peak feature in all three quantities of $\Delta P$ shows symmetrical features about the origin at $\pm H_r$, and the line shapes are strikingly similar to the ac MR line shapes. The sourced rf power (1 dBm for the impedance analyzer and 10 dBm for the VNA) is absorbed at a sample from the rf magnetic field is related to the imaginary part of the permeability, $\mu''$, according to the relation $P_{\text{ac}} = \frac{1}{2} V_0^2 \omega \mu''$, where $\omega = 2 \pi f$, $f$ is the frequency of current, and $V$ is the sample volume. The characteristic double peak feature in all three quantities of $\Delta P$, $\Delta P$, and $\Delta P$ shifts towards higher magnetic field values for higher frequencies of the signal as illustrated in the two-dimensional image plots shown in Figs. 2(e) and 2(f) for MR, MX, and $\Delta P$, respectively, as a function of $H_r$, and rf frequency ($f$); minima are depicted by dark green while maxima are depicted by yellow.

Equation (1) is valid for electromagnetic waves in which the electric and magnetic field components are in-phase. However, for electromagnetic waves propagating through a dispersive medium, the electric and magnetic field components become out of phase. In such a case, the power absorption spectrum will contain an additional dispersive term which can be described by an antisymmetric Lorentzian function. Considering the presence of both in-phase (symmetric Lorentzian function) and out-of-phase (antisymmetric Lorentzian function) components, the resultant power absorption by the sample can be expressed as

$$-\Delta P(H_d) = A_{\text{sym}} \frac{(\Delta H)^2}{(H_{dc} - H_1)^2 + (\frac{\Delta H}{2})^2} + A_{\text{asym}} \frac{\Delta H}{(H_{dc} - H_{res})^2 + (\frac{\Delta H}{2})^2} + C,$$

where $A_{\text{sym}}$ and $A_{\text{asym}}$ are the coefficients of symmetric and antisymmetric Lorentzian functions, respectively, and $C$ is a constant offset parameter. Similarly, the observed signals in MR and MX were also fitted with symmetric and antisymmetric Lorentzian components. It was found that MR was dominated by the antisymmetric component, while MX was dominated by the symmetric component. The peaks observed in MR coincide with the peaks in the derivative of X (or MX) with respect to magnetic field, as shown in the inset of Fig. 3(b), for $f = 2$ GHz. From these fits, the resonance field ($H_r$) was extracted and are presented in Fig. 3(b) for both the
Δ in both the techniques. Hence, the abrupt jumps observed in MR and impedance analyzer method and γ-factor. We obtain Δ/2π= 0.020 MHz/Oe for the stripcoil-impedance analyzer and Δ/2π= 0.023 MHz/Oe for stripcoil-VNA methods. The plot of ΔP vs H gives similar information regarding γ/2π, 4πMs, and Hk. Since no current flows through the sample (except for the induced current) when using the stripcoil, one can infer that the EPR signal is predominantly due to dynamic permeability changes caused by the hrf generated along the axis of the stripcoil rather than due to drastic changes in the scattering rate of electrons. Thus, the observed EPR features in direct MI measurement are confirmed to be caused by the field dependence of μ during resonance.

In summary, the magnetoimpedance of the La0.6Ca0.4MnO3 sample measured indirectly using a copper stripcoil and an impedance analyzer showed an abrupt increase at a critical value of μ which was confirmed by an independent measurement using a copper stripcoil and an impedance analyzer. Our present results confirm that the magnetic field dependence of the dynamic permeability of the sample arose mainly from the magnetic field dependence of the dynamic permeability of the sample and not due to the enhanced scattering of the eg electron.

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REFERENCES
1. C. P. Poole, Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques, 2nd ed. (Dover Publications, New York, 1996).
2. B. Stich, S. Grulich-Weber, and J.-M. Spatok, J. Appl. Phys. 77, 1546 (1995); For a recent review, see C. Boehme and H. Malissa, J. Magn. Magn. Mater. 13, 83 (2017).
3. S. Goennenwein, S. Schink, A. Brandmaier, A. Boger, M. Opel, R. Gross, R. Keizer, T. Klapwijk, A. Gupta, and H. Huebl, Appl. Phys. Lett. 90, 162507 (2007).
4. W. Egan and H. Juretschke, J. Appl. Phys. 34, 1477 (1963).
5. M. Harder, Z. Cao, Y. Gui, X. Fan, and C.-M. Hu, Phys. Rev. B 84, 054423 (2011).
6. M. Dobers, K. von Klitzing, J. Schneider, G. Weimann, and K. Ploog, Phys. Rev. Lett. 61, 1650 (1988).
7. U. Chaudhuri and R. Mahendiran, Appl. Phys. Lett. 115, 092405 (2019).
8. A. H. Morrish, The Physical Principles of Magnetism (Wiley; IEEE Press, 2001).
9. U. Chaudhuri, M. Kumari, and R. Mahendiran, IEEE Trans. Magn. 54, 1–4 (2018).
10. Y.-Y. Song, S. Kalarickal, and C. E. Patton, J. Appl. Phys. 94, 5103 (2003).
11. C. Kittel, Phys. Rev. 73, 155 (1948).
12. S. B. Oseroff, M. Torikachvili, J. Singley, S. Ali, S. W. Cheong, and S. Schultz, Phys. Rev. B 53, 6521 (1996).
13. A. Shengelaya, G. Zhao, H. Keller, K. A. Muller, and B. I. Kochelaev, Phys. Rev. B 61, 5888 (2000).
14. A. I. Shames, E. Rosenberg, G. Gorodetsky, and Ya. M. Mukovskii, Phys. Rev. B 68, 174402 (2003).