Electron Spin Resonance Study on \( \text{Nd}_{0.7}(\text{Sr}_{0.3-x}\text{Ca}_x)\text{MnO}_3 \)

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Electron spin resonance (ESR) spectra of \( \text{Nd}_{0.7}(\text{Sr}_{0.3-x}\text{Ca}_x)\text{MnO}_3 \) powders (0 \( \leq x \leq 0.3 \)) have been measured over the range of temperature between 110 and 290 K. While for \( x = 0.2, 0.25 \) and 0.3 only one absorption line (Line I), corresponding to a \( g \)-value around 2, was observed while for \( x = 0 \) and 0.1 an additional line (Line II) was observed below the magnetic transition temperature. Based on the temperature dependent \( g \)-values and \( \Delta H \), we have assigned the ESR signal of Line I to the \( \text{Mn}^{4+} \)-ions, while that of Line II to the ferromagnetic resonance due to the ferromagnetic coupling between \( \text{Mn}^{4+} \) and \( \text{Mn}^{3+} \).

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I. Introduction

Since the observation of the colossal magnetoresistance (CMR) effect in the ferromagnetic compound \( \text{La}_{1-x}\text{A}_x\text{Mn}[1] \) many attempts were made to understand the mechanism of CMR. The proposed models include strong electron-phonon coupling \([2,3]\), Jahn-Teller (J-T) effect \([4]\), and polaron formation \([5]\). However, a complete understanding of the origin of CMR calls for a fuller experimental evidence. And, in our opinion, electron spin resonance (ESR) spectra could provide important information, regarding the issues of the homogeneity of the sample \([6]\), the spin-dynamic \([7]\), and the J-T polaron formation \([8]\). In this study, we investigate the ESR spectra on a series of \( \text{Nd}_{0.7}(\text{Sr}_{0.3-x}\text{Ca}_x)\text{MnO}_3 \) powder samples. By replacing \( \text{Sr}^{2+} \) with \( \text{Ca}^{2+} \)-ion, the valence of the Mn-ions were not changed. Instead, owing to the mismatch between the size of \( \text{Sr}^{2+} \) and \( \text{Ca}^{2+} \), the crystal lattice is distorted, with bent of Mn-0-Mn bond angles \([9]\). The changing of the bond angles, in turn, affects the magnetic and resistive properties significantly. We, therefore, believe that our ESR study on this system could shed some light on the size effect on the spin-activity of the Mn-ions.

II. Experiment

\( \text{Nd}_{0.7}(\text{Sr}_{0.3-x}\text{Ca}_x)\text{MnO}_3 \) powders with \( x = 0, 0.1, 0.2, 0.25 \) and 0.3 were prepared by the standard solid-state reaction method. The x-ray diffraction analysis was carried out with a Scientag (xl) diffractometer (\( \text{CuF}_2 \) radiation) to check the phase purity. The
Curie temperatures ($T_c$) of the samples were determined from the magnetization ($M$) vs. temperature ($T$) curve by a commercial Quantum Design SUQID magnetometer. The electron spin resonance (ESR) spectra were taken with a BRUCKER EMX system operated at 9.48 GHz, and the field sweep was from 50 to 10000 Gauss, with samples placed at the center of a TE$_{102}$ rectangular cavity. The temperature range was from 290 down to 110 K.

III. Results and discussions

Based on the x-ray diffraction patterns all samples are identified to be single-phased orthorhombic, with the Pbnnm space group. The magnetic transition temperatures ($T_c$) are 270, 220, 140, 130 and 120 K for samples with Ca-concentration ($x$) = 0, 0.1, 0.2, 0.25 and 0.3, respectively. For $x$ = 0.2, 0.25 and 0.3, we have obtained only one ESR line (Line I), while for $x$ = 0 and 0.1, an additional line (Line II) has been observed near and below $T_c$. The ESR spectra for $x$ = 0, at 290 K (the upper one) and at 270 K (the lower one) are displayed in Fig. 1. The plot shows clearly the existence of a second line at $T_c$ ($T_c$ = 270 K) which we identified as a ferromagnetic resonance line. Similar results were obtained for $x$ = 0.1. We have employed the Lorentzian fit to analyze our integrated resonance spectra and defined $H_r$ to be the central field of the resonance absorption peak and $AH$ the half-way width of the Lorentzian distribution curve. After the values of $H_r$ were obtained we used the simple equation $h \nu = g_{	ext{L}} \mu_B H_r$ to calculate the $g$-value. Here $h$ is the Plank constant, $\nu$ the frequency of the microwave, and $\mu_B$ the Bohr magnetron. Figures 2 and 3 show $g$-value vs. $T$ for Line I and Line II, respectively. As seen in Fig. 2, the $g$-value is around 2.0 for all-samples at 290 K; it increases with decreasing temperature owing to the presence of exchange fields which are proportional to the magnetization. For $x$ = 0.2, 0.25 and 0.3 the increase is slight to about 2.1 at $T$ = 110 K. For $x$ = 0 the available data goes down to only 230 K, below this temperature the spectrum becomes too broad. For $x$ = 0.2, 0.25 and 0.3, the $g$-value increases sharply with $T$ down to 160 K, then the line becomes too broad to be analyzed. In Fig. 3, the $g$-value of Line II increases with decreasing $T$ for $x$ = 0 and 0.1. The $g$-values range from 2.4 to 6.5. Figures 4 and 5 are the plots of $AH$ vs. $T$ for Line I and Line II, respectively. As shown in Fig. 4, the $AH$-$T$ curves behave differently for different samples. For $x$ = 0, $AH$ increases with decreasing temperature, then becomes too broad below 220 K. For $x$ = 0.2 to 0.3, $AH$ more or less decreases with decreasing $T$. In Fig. 5, $AH$ of Line II for both $x$ = 0 and 0.1 increases with increasing $T$.

In order to understand the physical meaning of Line I and Line II, we have to first clarify the origin of the ESR (Electron Spin Resonance) signal in manganese perovskites. As pointed out by Shengelaya et al. [8], Mn$^{3+}$ ($3d^4$ with $s = 2$) is unlikely to have an observable ESR signal since it exhibits a large zero-field splitting and strong spin-lattice relaxation. It was suggested therefore that the observed ESR signal in (La, Ca)MnO$_3$ compounds is mainly from the Mn$^{4+}$-ion ($3d^3$ with $s = 3/2$), though not from isolated Mn$^{4+}$ ions. The $g$-value of an Mn$^{4+}$-ion in an octahedral field is 1.994 [10], which is close to what we have obtained for Line I. We thus assign Line I to the electron paramagnetic (EPR) signal of the Mn$^{4+}$-ion. Since Line II was only observed below $T_c$, it should be related to ferromagnetic coupling between the Mn$^{4+}$ and the Mn$^{3+}$-ion. We thus assign Line II to the ferromagnetic resonance (FMR) signal of the Mn$^{4+}$-Mn$^{3+}$ clusters. The
FIG. 1. The electron spin resonance (ESR) for a Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ powder sample, at 290 K (upper one) and 270 K (lower one), respectively.

FIG. 2. $g$-value of Line 1 vs. temperature ($T$) for Nd$_{0.7}$(Sr$_{0.3}$-xCax)MnO$_3$ with $x = 0$, 0.1, 0.2, 0.25 and 0.3, respectively.

FIG. 3. $g$-value of Line II vs. temperature ($T$) for Nd$_{0.7}$(Sr$_{0.3}$-xCax)MnO$_3$ with $x = 0$ and 0.1, respectively.

FIG. 4. $\Delta H$ of Line I vs. temperature ($T$) for Nd$_{0.7}$(Sr$_{0.3}$-xCax)MnO$_3$ with $x = 0$, 0.1, 0.2, 0.25 and 0.3, respectively.

The reason we did not observe Line II for $x = 0$, 0.25 and 0.3 is that the measured temperature range may be $> T_c$.

In the EPR results of (La, Ca)MnO [8] an increase of $\Delta H$ with decreasing temperature for $T < T_c$ was observed, and the broadening is associated with a critical "slowing down" of the spin fluctuations in a ferromagnet. We therefore find the increase of the $\Delta H$ of Line II with decreasing $T$ (see Fig. 5) to be of the same origin. The large variability of the $T$-dependence of $\Delta H$ for Line I (see Fig. 4) is still not understood. We only speculate that it may be associated with the insulating to metallic transition of these samples.

IV. Conclusion

We have investigated the temperature dependent ESR spectra for a series of Nd$_{0.7}$
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FIG. 5. $\Delta H$ of Line II vs. temperature (T) for Nd$_{0.7}$(Sr$_{0.3-x}$Ca$_x$)MnO$_3$ with $x = 0$ and 0.1, respectively.

$\text{(Sr}_{0.3-x}\text{Ca}_{x})\text{MnO}_3$ powder samples, with $x = 0$, 0.1, 0.2, 0.25 and 0.3. The ESR spectra for $x \leq 0.2$, 0.25 and 0.3 show only one absorption line (Line I). The Line I was found to correspond to $g = 2$ for all samples at 290 K and we attributed it to the EPR signal of the Mn$^{4+}$ ions. The ESR spectra for $x = 0$ and 0.1 below $T_c$ imply that there exist isolated Mn$^{4+}$ clusters below $T_c$. The additional absorption line (Line II) observed for $T > T_c$ in these samples is believed to be due to ferromagnetic coupling between Mn$^{3+}$ and Mn$^{4+}$ ions. We have also observed a broadening of the linewidth of Line II with decreasing $T_c$, and associated it with a critical slowing down of the spin fluctuations.

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References