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LETTER TO THE EDITOR

Exchange-narrowing spin–spin interaction in the paramagnetic regime of perovskite manganites studied through the EPR measurements for $(La, Y)_{2/3}(Ca, Sr, Ba)_{1/3}MnO_3$ with a wide span of T_c

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Abstract. The electron paramagnetic resonance (EPR) spectrum as a function of T is experimentally studied for $(La, Y)_{2/3}(Ca, Sr, Ba)_{1/3}MnO_3$ with a wide span of T_C. In the real paramagnetic regime ($T \geqslant T_{min}$), the spectrum consists of a single line with the resonance field being independent of T. The resonance linewidth is given by $\Delta H_{pp} = \Delta H_{pp,min} + b(T - T_{min})$. The exchange-narrowing spin–spin interaction and the spin–lattice interaction are explained to be responsible for the terms of $\Delta H_{pp,min}$ and $b(T - T_{min})$, respectively. Based on the exchange-narrowing mechanism, the values of $\Delta H_{pp,min}$ are directly deduced from the T_C-values, which are well consistent with the experimental $\Delta H_{pp,min}$-values. This confirms the possibility that the exchange-narrowing spin–spin interaction exists in the ABO_3-type perovskite manganites.

Among the ABO_3-type perovskite manganites $(L, B)MnO_3$ (Ln being a rare earth ion and B a divalent alkali), $Ln_{2/3}B_{1/3}MnO_3$ has been widely studied [1]. The system with $\langle r_A \rangle \geqslant \langle r_A \rangle_L$ ($\approx$1.18 Å) is known to undergo a transition from paramagnetic insulating (PMI) to ferromagnetic metallic (FMM) states when temperature is decreased, where $\langle r_A \rangle$ and $\langle r_A \rangle_L$ are the average A-site ionic size and the A-site ionic size limit, respectively. Associated with the transition, one observes a resistance maximum versus temperature, at a temperature T_p which coincides with the Curie temperature T_C deduced from the $M(T)$ curves registered in low magnetic fields (typically 10^{-2} T). Applying magnetic fields largely suppress the resistance, leading to an observation of the so-called colossal magnetoresistance (MR) effect, and the largest MR effect appears at T around T_C. The magnetic and electrical properties have been traditionally understood in terms of the double-exchange (DE) model proposed by Zener [2]. However, recent theoretical considerations [3] indicated that the DE model alone cannot quantitatively account for the observed large MR values. Various mechanisms have been proposed to explain the observed colossal MR effects; however, their true nature is still a subject under intense investigation.

In order to test the correct mechanism dealing with the colossal MR effect, it is necessary to study the spin dynamic behaviour in the paramagnetic (PM) phase of manganese oxides. For this purpose, several reports on the measurements of electron paramagnetic resonance

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(EPR) have been presented [4–10]. It is commonly found that these oxides show strong EPR signals with large variations of the line parameters as a function of T. In every case, a common feature of the T-dependent linewidth $\Delta H_{pp}(T)$ is revealed, i.e., with decreasing T, ΔH_{pp} decreases, passes through a minimum at T_{min} and then substantially increases on further decreasing T. Various relaxation mechanisms have been proposed to explain the observed broadening of the resonance line with T, including the bottlenecked spin relaxation [5] and the single-phonon spin–lattice relaxation [6, 11]. It has been also suggested that a mechanism involving the phonon-modulated DE interaction via dynamic Jahn–Teller effect may be more appropriate for this kind of manganese oxides [6]. In this letter we report a systematic study of EPR in a series of perovskite compounds $(La, Y)_{2/3}(Ca, Sr, Ba)_{1/3}MnO_3$ with T_C basically covering the whole PMI-to-FMM phase line proposed by Hwang *et al* [1]. Our results demonstrate that the linewidth minima measured in different materials can be directly deduced from the corresponding experimental T_C-values according to the exchange-narrowing mechanism [12]. This confirms the possibility that the exchange-narrowing spin–spin interaction exists in perovskite manganites.

Three single-phase powder ceramic samples with nominal compositions of $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$, $La_{1/2}Ca_{1/3}MnO_3$ and $La_{2/3}Ba_{1/3}MnO_3$ were used in the present study that were fabricated by the standard solid state reaction. Details of fabrication for each sample are similar to those commonly described in the literature. The phase purity for each sample was checked by x-ray diffraction and no spurious phase was found. Resistance was measured by the standard four-probe method on cooling from room temperature to LHe temperature. The EPR experiments were performed at 9.46 GHz using a Bruker (ER-200D-SRC) reflection X-band type spectrometer. Each EPR spectrum was measured at given temperature by sweeping magnetic field from 0 to 6000 Oe. The temperature for each ESR measurement was controlled to an accuracy of ± 0.1 K using the Bruker N_2 temperature controller.

The measurement of resistance as a function of T shows that all the studied samples undergo a transition from semiconductor to metal at a temperature T_p. In figure 1 we superpose the obtained T_p as a function of $\langle r_A \rangle$ onto the general phase diagram proposed by Hwang *et al* [1] for the systems $Ln_{1-x}B_xMnO_3$ ($x \sim 1/3$). It can be found that our results agree well with their phase diagram. From their studies, the T–$\langle r_A \rangle$ phase diagram in the region of $\langle r_A \rangle \geqslant \langle r_A \rangle_L$ ($\approx$1.18 Å) is separated into two distinguishable regions: PMI and FMM. For this reason, we approximate the T_p determined by the measurement of zero-field resistance versus temperature as the Curie temperature T_C, although we do not perform the measurement of magnetization for the present samples. In this figure as well as in the following figures dealing with ESR experiments we also present the data obtained in $La_{2/3}Sr_{1/3}MnO_3$ by Causa *et al* [7]. This sample together with our three samples mentioned above basically cover the whole phase diagram for the PMI-to-FMM transition proposed by Hwang *et al* [1].

The EPR spectra were measured at various constant temperatures ranging from 435 K to T_C for each sample. Here the recorded signal is an ESR absorption-derivative signal. As an example, the spectra measured in $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$ are shown in figure 2. This sample has a lower $T_C \sim 89$ K, therefore, the experimental temperature covers a very wide temperature range from $\sim 5T_C$ to $\sim T_C$. Our experiments indicate that all samples show a similar behaviour in ESR signal: at high temperatures, the spectrum consists of a single line which has a Lorentzian lineshape. The resonance field corresponds a g-value close to that of the free electron ($g_e = 2.0023$) and independent of temperature. The derivative signal intensity greatly increases with decreasing T. The symmetric signal with the Lorentzian lineshape is maintained to a temperature T_{min}. Below this temperature some distortions of the lineshape occur: with decreasing temperature from T_{min}, the derivative signal intensity becomes weak, the resonance line broadens and the resonance field shifts to lower field.

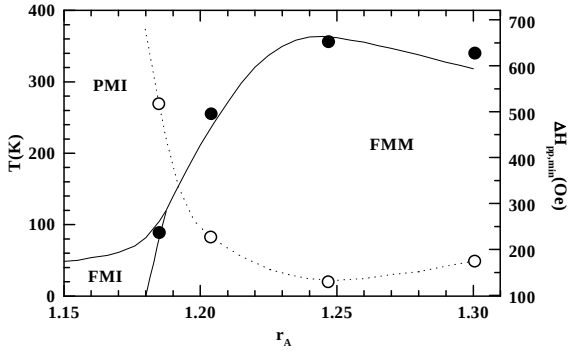

Figure 1. Phase diagram of temperature against A-site ionic size for the system $Ln_{1-x}B_xMnO_3$ ($x \sim 1/3$), where Ln is a trivalent rare-earth ion and B is a divalent alkali-earth ion (after Hwang *et al* ([1])). Superimposed solid circles represent the data on $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$, $La_{1/2}Ca_{1/3}MnO_3$ and $La_{2/3}Ba_{1/3}MnO_3$ from the present work as well as on $La_{2/3}Sr_{1/3}MnO_3$ from the work in [6]. The open circles represent the values of the linewidth minimum, $\Delta H_{pp,min}$, which are obtained from the experimental $\Delta H_{pp}(T)$ for the above four samples.

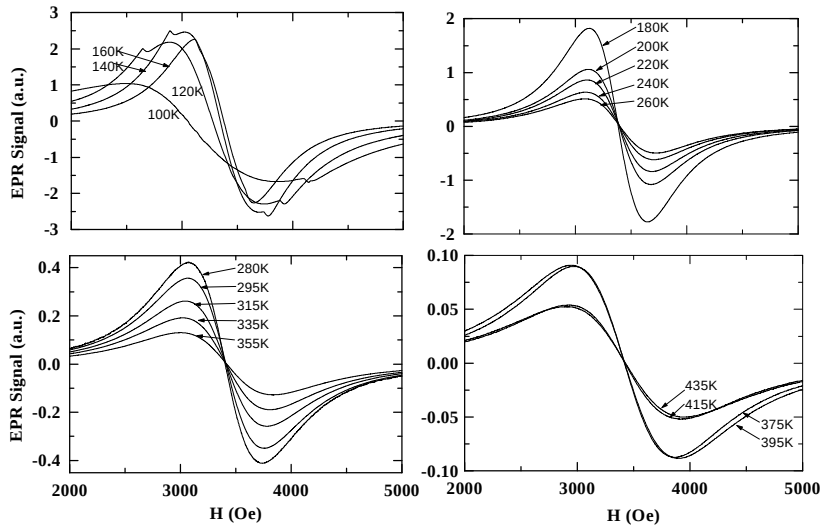

Figure 2. EPR spectrum as a function of T for $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$.

Shown in figure 3 is ΔH_{pp}, the peak-to-peak linewidth in the derivative curve as a function of T for the three samples. All samples show a common feature in the ΔH_{pp}–T curve: The ΔH_{pp} decreases almost linearly with decreasing T in the range of $T > T_{min}$, and shows a minimum at T_{min}. On further decreasing T from T_{min}, ΔH_{pp} greatly increases. It is interesting that the T_{min} corresponding to a minimum in the ΔH_{pp}–T curve is the same as the temperature below which some distortions of the lineshape occur. For $La_{1/2}Ca_{1/3}MnO_3$, T_C is determined to be ∼250 K, while $T_{min} \sim 300$ K. It happens that T_{min} is just around 1.2 T_C. Because of this fact, it is often mentioned in the literature that the linewidth shows a minimum at $T_{min} \sim 1.2\ T_C$. However, we would like to point out that such a statement is inaccurate. In fact, in the previous report [7] on $La_{2/3}Sr_{1/3}MnO_3$ the linewidth minimum was found to appear at $T_{min} \sim 1.04\ T_C$, while for $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$ T_{min} (∼180 K) is much higher than

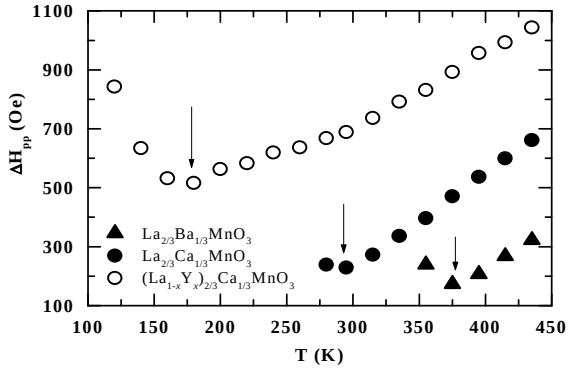

Figure 3. Peak-to-peak linewidth as a function of T for the three samples of $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$, $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Ba_{1/3}MnO_3$.

T_C (∼89 K). A possible interpretation for the difference between T_{min} and T_C was previously proposed in terms of some magnetic inhomogeneity in materials [8]. This can be confirmed in the present measurements. As seen in figure 2, the distortions of the lineshape start to occur just below T_{min}, but above this temperature the spectrum shows a single line with no structure. From this observation, we believe that a real PM state is in the temperature range $T > T_{min}$.

In the real PM region, as found in figure 3, the linewidth as a function of T approximately shows a linear behaviour for the three studied samples. For the sake of the following discussion, we can write $\Delta H_{pp}(T)$ in two terms:

$$\Delta H_{pp} = \Delta H_{pp,min} + b(T - T_{min}) \tag{1}$$

where $\Delta H_{pp,min}$ is the linewidth at T_{min} corresponding to a minimum value in the ΔH_{pp}–T curve and b is a material-dependent constant. The first term is independent of T and caused by the exchange-narrowing spin–spin interaction, which will be discussed in the following. The second term should be attributed to the T-dependent spin–lattice interaction. The latter has been discussed by different groups [5, 6, 8, 9] from different mechanisms including the single-phonon spin–lattice relaxation [11] and the bottlenecked spin relaxation between Mn^{3+} and Mn^{4+} magnetic subsystems [5] etc. These mechanisms can account for the linear or quasilinear T dependence of ΔH_{pp}, although the physical origin for the relaxation process is different between different mechanisms.

Here we are interested in the study of T-independent ESR line broadening. Clearly, the T-independent broadening strongly depends on materials. We plot $\Delta H_{pp,min}$ in figure 1 as a function of $\langle r_A \rangle$ together with the T–$\langle r_A \rangle$ phase diagram for the perovskite manganites $Ln_{2/3}B_{1/3}MnO_3$. It can be seen that the smallest value of $\Delta H_{pp,min}$ is observed in the system of $La_{2/3}Sr_{1/3}MnO_3$ with the highest T_C, while for the other systems the $\Delta H_{pp,min}$-value greatly increases with decreasing T_C. If we calculate the product $\Delta H_{pp,min}T_C$, we find that the product almost keeps constant for different samples. A similar phenomenon can be also found if we examine the previously reported data in the systems $(La_{1-x}Gd_x)_{2/3}Ca_{1/3}MnO_3$ [9] or $Pr_{0.7}(Sr_{1-x}Ca_x)_{0.3}MnO_3$ [10]. Associated with the doping of smaller Gd^{3+} ions in La^{3+} sites or smaller Ca^{2+} ions in Sr^{2+} sites, T_C decreases while $\Delta H_{pp,min}$ increases. The correlation between T_C and $\Delta H_{pp,min}$ makes us think of the previous consideration in a concentrated paramagnet in which the ESR line broadening is dominated by the exchange-narrowing spin–spin interaction. The mechanism predicts an exchange-narrowed width ΔH_0 with the following

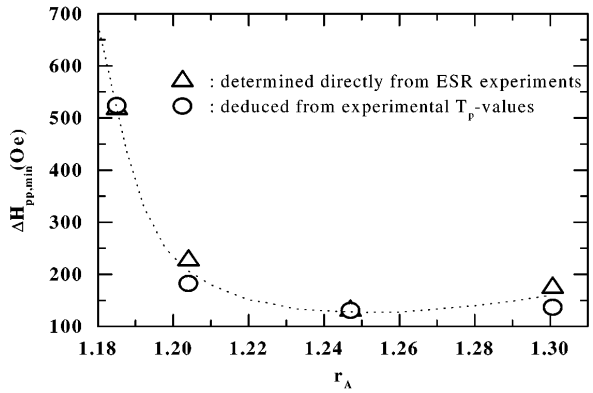

Figure 4. Linewidth minimum as a function of A-site ionic size: the experimental $\Delta H_{pp,min}$-data (△) and the calculated values (○) directly from the experimental T_C-values according to the exchange-narrowing mechanism which is explained in the text. The dotted line is a guide to the eyes.

form

$$\Delta H_0 = (\Delta H_{dip})^2 / H_{ex}. \tag{2}$$

Here ΔH_{dip} is the dipolar width, H_{dip} is the dipolar field experienced by each spin from all its neighbouring spins and H_{ex} is the exchange field. H_{ex} is related to the Curie temperature T_C through the relation: $S\mu_B H_{ex} = k_B T_C$, where S is the effective spin. Replacing this into equation (2), the exchange-narrowed width ΔH_0 can be rewritten by

$$\Delta H_0 = S\mu_B(\Delta H_{dip})^2 / k_B T_C. \tag{2'}$$

This predicts a dependence of ΔH_0 versus T_C similar to the present experimental observation for $\Delta H_{pp,min}$ versus T_C. Because of this fact, it is reasonable to identify $\Delta H_{pp,min}$ with the exchange-narrowed width ΔH_0. The resonance broadening observed in the real PM region is then explained as follows. At T_{min}, the broadening is caused by the exchange-narrowing spin–spin interaction. When T is higher than T_{min}, the additional contribution arising from the spin-lattice interaction leads to a linear increase of ΔH with T.

In order to confirm the above consideration, we directly calculate $\Delta H_{pp,min}$ from the experimental T_C-value according to equation (2′). The effective spin of Mn ions is 1.83 for the present systems in which the proportions of Mn^{3+} ($t_{2g}^3 e_g^1$, $S = 2$) and Mn^{4+} ($t_{2g}^3 e_g^0$, $S = 3/2$) ions are 67% and 33%, respectively. The calculated results are plotted in figure 4 together with the experimental data. It can be seen that the calculated results are well consistent with the experimental values. This agreement demonstrates that the ABO_3-type perovskite manganates in their PM regions have behaviour similar to that in conventional concentrated magnetic materials in which the resonance linewidth can be exchange narrowed. It is worthwhile to point out that the same value of ΔH_{dip} ($\sim 2 \times 10^4$ Oe) is used in our calculation for the four studied samples. This implies that an increase (decrease) of the DE interaction raises (lowers) T_C, but does not significantly influence the dipolar field experienced by each spin from all its neighbouring spins.

In summary, we have measured the ESR spectrum as a function of temperature for three samples $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$, $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Ba_{1/3}MnO_3$. Together with the previous study on $La_{2/3}Sr_{1/3}MnO_3$, the span of T_C for the four samples basically covers the whole phase line from PMI to FMM states proposed by Hwang *et al* [1]. Our results show

that a real PM state appears in the temperature range $T > T_{min}$. The ESR spectrum observed in the real PM region consists of a single line with a Lorentzian lineshape and the resonance field is independent of T. Based on the analysis of linewidth, we propose that both the exchange-narrowing spin–spin interaction and the spin-lattice interaction are responsible for the resonance line broadening. The linewidth minima deduced from the T_C-values according to the exchange-narrowing mechanism are well consistent with the experimental $\Delta H_{pp,min}$-values. This confirms our consideration that besides the T-dependent spin–lattice interaction, the exchange-narrowing spin–spin interaction plays an important role in dominating the resonance broadening in the ABO_3-type perovskite manganates.

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