EPR in $La_{1-x}Ca_xMnO_3$: Relaxation and bottleneck

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Recent EPR and susceptibility measurements in $La_{1-x}Ca_xMnO_3$ support the existence of a bottleneck EPR regime up to 1000 K quantitatively. The EPR linewidth and electrical conductivity follow the same temperature dependence in the range of 250 to 650 K predicted by the small polaron hopping model. This indicates that spin-lattice relaxation in manganates is due to the relaxation of spins of e_g Jahn-Teller polarons to the lattice.

Electron paramagnetic resonance (EPR) is a powerful technique to study static and dynamic magnetic correlations on a microscopic level and can help to clarify the complex magnetic state in doped manganese perovskites. Recently Oseroff *et al.*[1] reported the first observation of an EPR signal in $La_{1-x}Ca_xMnO_{3+y}$ with different Ca and oxygen content. These mixed-valent manganese oxides are known to exhibit a large (called colossal) magnetoresistive effect.[2] The authors in Ref. 1 ascribed the observed EPR signal to some complex spin entity, resulting from a collection of Mn^{3+} and Mn^{4+} ions. However, the exact nature of the paramagnetic center responsible for the EPR signal remained unknown. In a previous paper[3] we reported a large oxygen isotope effect on the EPR linewidth and the intensity in ^{16}O and ^{18}O isotope substituted $La_{1-x}Ca_xMnO_{3+y}$. We proposed a model in which a bottlenecked spin relaxation takes place from the exchange-coupled constituent Mn^{4+} ions via the Mn^{3+} Jahn-Teller ions to the lattice. This model provides a reasonable explanation of the observed EPR signal as well as on the observed isotope effects.

Very recently Causa *et al.*[4] performed EPR and dc susceptibility measurements in several Mn perovskites up to 1000 K. They carefully analyzed the EPR intensity quantitatively and came to the conclusion that all Mn spins contribute to the EPR signal in the temperature range studied. We would like to point out that this conclusion is in agreement with the bottleneck model. Indeed, the bottleneck phenomenon involves the onset of a collective motion of the total magnetic moments of the Mn^{4+} and Mn^{3+} spin systems. Therefore, in the bottleneck regime the EPR intensity is proportional to the total susceptibility $\chi_{\rm tot}$ of the Mn^{4+} and Mn^{3+} spins:

$$I_{\rm EPR} \propto \chi_{\rm tot} = \chi_s + \chi_\sigma , \tag{1}$$

where χ_s and χ_σ are the renormalized static susceptibilities of the Mn^{4+} and Mn^{3+} spin systems, respectively,[5]

$$\chi_s = \chi_s^0 \frac{1+\lambda\chi_\sigma^0}{1-\lambda^2\chi_\sigma^0\chi_s^0}, \quad \chi_\sigma = \chi_\sigma^0 \frac{1+\lambda\chi_s^0}{1-\lambda^2\chi_\sigma^0\chi_s^0}. \tag{2}$$

Here χ_s^0 and χ_σ^0 are the bare (without exchange) susceptibilities of the Mn^{4+} and Mn^{3+} ions and the factor λ is a dimensionless exchange coupling constant between them. According to Eq. (2) the denominators in χ_s and χ_σ are the same and because $\lambda^2\chi_\sigma^0\chi_s^0 \sim 1$, the temperature dependences of both terms are dominated by their denominators, so that χ_s has nearly the same temperature dependence as χ_σ. Therefore, despite the fact that in Ref. 3 we used only χ_s to fit the temperature dependence of EPR intensity, the conclusion of Ref. 3 remains valid. However, it is necessary to take into account both χ_s and χ_σ in order to explain the EPR intensity more quantitatively. Thus the results of Causa *et al.*[4] support our interpretation for the existence of the bottleneck effect up to at least 1000 K.

Now the question arises: why does the bottleneck regime survive up to such a high temperature? In order to answer this question let us consider the electronic structure of manganites. Doped manganese perovskites are mixed-valent systems containing $Mn^{3+}(3d^4)$ and $Mn^{4+}(3d^3)$ ions. The Mn^{3+} ions have three electrons in the t_{2g} state and one electron occupies the double-degenerate e_g level which is split due to the Jahn-Teller effect by $E_{\rm JT}$. The hopping of the e_g electron from a $Mn^{3+}{:}t_{2g}^3e_g^1$ to a $Mn^{4+}{:}t_{2g}^3e_g^0$ ion is responsible for the electronic conduction, whereas the t_{2g}^3 electrons remain localized with a core spin $S=3/2$ (see Fig. 1). The strong Hund coupling between the t_{2g} spins and the e_g spins of the carriers orients them parallel to each other. The Hund coupling, J_H is large, of the order of ~ 1 eV. In our opinion, the Hund coupling, which is much larger than the spin-lattice relaxation rate, is the reason why the bottleneck regime survives up to 1000 K.

The bottleneck effect in EPR was first investigated in copper and gold metals doped with paramagnetic *S*-state Mn^{2+} ions (see, for example, an excellent review by Barnes[5]). The bottleneck regime exists if the relaxation of the localized spin to the lattice occurs via the conduction electrons rather than its own week *S*-state interaction to the lattice. In the manganates the spins in the half-filled t_{2g} subshell play the role of *S*-state localized spins and the e_g electrons behave in the same way as the conduction electrons in the metals.

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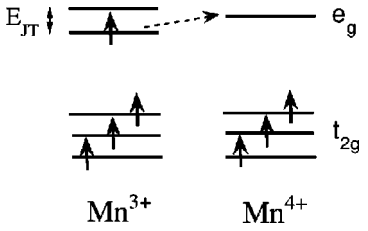

FIG. 1. The schematic electronic structure of the e_g and t_g levels of Mn^{3+} and Mn^{4+} ions.

In a previous paper[3] we showed that the bottleneck model can explain the temperature dependence of the EPR intensity of $La_{1-x}Ca_xMnO_{3+y}$ up to approximately 500 K. Above this temperature a deviation of the theoretical fit from the experimental data occurs. We previously attributed this behavior to a gradually opening of the bottleneck and to the transition to the isothermal regime.[3] However, recent results of Causa *et al.*[4] indicate that the bottleneck effect persists up to at least 1000 K. Therefore, another possibility has to be considered. First of all one should note that in the fitting procedure of the temperature dependence of the EPR intensity, we assumed the fitting parameter J (ferromagnetic double exchange integral) to be temperature independent. However, recent small-angle neutron scattering experiments demonstrated that below $\sim 2T_c$ small ferromagnetic clusters start to form in $La_{0.67}Ca_{0.33}MnO_3$ (Ref. 6). It is very likely that the formation of such clusters may modify the double-exchange interaction. This may be the reason why it was not possible to fit $I(T)$ over the entire temperature range using a single temperature independent value of the exchange integral J.

In the following we discuss the temperature dependence of the EPR linewidth ΔH_{pp}. Figure 2(a) shows the temperature dependence of the EPR linewidth for the sample with $x=0.2$. The linewidth has minimum near T_c and increases with increasing temperature. Trying to explain the temperature dependence of ΔH_{pp} above $T_{\min}$, we noticed that it is very similar to the temperature dependence of the electrical conductivity observed in manganates.[7] The solid line in Fig. 2(a) represents the best fit to the data using the expression

$$\Delta H_{pp}(T)=\Delta H_0+\frac{A}{T}\exp(-E_a/k_BT). \tag{3}$$

The following fitting parameters were obtained: $\Delta H_0 = 80(8)$ G, $A=5.0(1)\times 10^6$ G K, and $E_a=0.106(1)$ eV.

In Fig. 2(a) we plotted for comparison the temperature dependence of the electrical conductivity measured by Worledge *et al.* in $La_{0.67}Ca_{0.33}MnO_{3+y}$ thin film.[8] This thin film had a ferromagnetic ordering temperature $T_c=203$ K close to our polycrystalline sample with $T_c=215$ K. One can see that the EPR linewidth and conductivity show similar temperature dependence. In the paramagnetic regime the conductivity σ of manganites is dominated by the adiabatic hopping motion of small polarons[8] with a temperature dependence of the form $\sigma(T)\propto 1/T\exp(-E_\sigma/k_BT)$. Figure 2(b) shows the linewidth and conductivity data plotted as $\ln(\Delta H_{pp}T)$ and $\ln(\sigma T)$, respectively, versus $1000/T$. As one can see both ΔH_{pp} and σ follow the same temperature dependence characteristic for the adiabatic hopping motion of small polarons with a similar values of the activation energy.

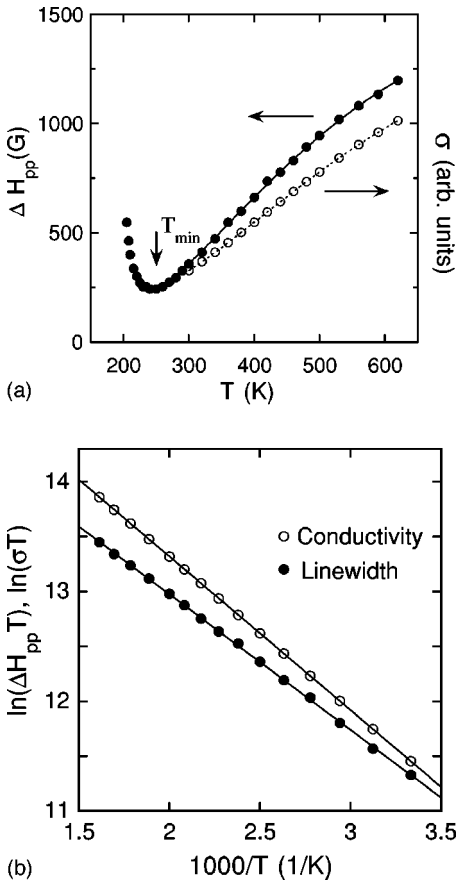

FIG. 2. (a) Temperature dependence of the EPR linewidth ΔH_{pp} for $La_{0.8}Ca_{0.2}MnO_{3+y}$ shown together with the temperature dependence of conductivity from Ref. 8. The solid line represents the best fit to the linewidth data above $T_{\min}$, using the expression $\Delta H_{pp}(T)=\Delta H_0+(A/T)\exp(-E_a/k_BT)$. The dotted line is a fit to the conductivity data using the adiabatic small polaron hopping model. (b) EPR linewidth and conductivity data same as in (a) plotted as $\ln(\Delta H_{pp}T)$ and $\ln(\sigma T)$, respectively, vs $1000/T$. The solid lines are linear fits indicating that both quantities follow the temperature dependence characteristic for the adiabatic hopping motion of small polarons with a similar value of the activation energy.

A proportionality between the EPR linewidth and the conductivity is often observed in systems with hopping conductivity.[9] It was shown that the hopping rate of the charge carriers limits the lifetime of the spin state. This leads to a broadening of the EPR line, proportional to the hopping rate and thus to the conductivity.[10] In this case the conductivity is determined by the probability of e_g electron hopping between nearest sites W. The hopping takes place with conserving the total spin and therefore will not lead to EPR relaxation. A broadening of the EPR line arises due to the hopping of the e_g electrons via the spin-orbit coupling. The probability of hopping between the nearest sites with changing the spin can be estimated as $W_s=W(g-2)^2$. The g-factor of EPR line in manganates is very close to 2. Therefore the condition for the bottleneck regime $W_s \ll W$ is satisfied automatically.

It should be noted that in the strong bottleneck regime the prefactor A in Eq. (3) contains a ratio of spin susceptibilities $\chi_\sigma/\chi_{\rm tot}$, where χ_σ is the bare susceptibility of Mn^{3+} ions and $\chi_{\rm tot}$ is total susceptibility. The temperature dependence

of χ_σ can be taken from the measurements of undoped $LaMnO_3$. According to Causa *et al.*[11] $\chi_\sigma = C/(T - T_{cw})$ with $T_{cw} = 220$ K. χ_{tot} can be found from the EPR intensity measurements in $La_{0.8}Ca_{0.2}MnO_3$ and fit with a Curie-Weiss law gives $T_{cw} = 218$ K (Ref. 7). Thus the ratio $\chi_\sigma/\chi_{\text{tot}}$ is practically temperature independent and will not affect the temperature dependence of the EPR linewidth.

The observed similarity between temperature dependencies of the EPR linewidth and the conductivity indicates that the spin-lattice relaxation is determined by the small polaron hopping. It is important to note that the activation energy $E_a = 0.106(1)$ eV, deduced from the present EPR linewidth data, is very close to the value $E_\sigma = 0.121(1)$ eV obtained from resistivity data of a $La_{0.67}Ca_{0.33}MnO_{3+y}$ thin film.[8] Moreover, one should emphasize that the value of E_a is nearly equal to the energy gap $E_g = 0.108$ eV determined from tunneling experiments on the $La_{0.8}Ca_{0.2}MnO_{3+y}$ thin film.[12]

To summarize, in this paper we discussed recent EPR experiments in CMR manganites[4] in terms of a model in which a bottlenecked spin relaxation takes place from the exchange-coupled constituent t_{2g} spins via the e_g charge carriers to the lattice. We have demonstrated that the bottleneck model provides an excellent description of the EPR data obtained in manganates up to 1000 K. Furthermore, the temperature dependence of the EPR linewidth is shown to have a similar temperature dependence as the electrical conductivity and is determined by the hopping rate of the e_g charge carriers.

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