EPR Evidence of Jahn-Teller Polaron Formation in $La_{1-x}Ca_xMnO_{3+y}$

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The electron paramagnetic resonance (EPR) signal in the mixed valence perovskite $La_{1-x}Ca_xMnO_{3+y}$ was investigated in the paramagnetic regime for ^{16}O and ^{18}O isotope substituted compounds. The characteristic differences observed in EPR intensity and linewidth for the two isotope samples can be explained by 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. For $x = 0.2$ the ferromagnetic exchange energy J exhibits a $^{16}O/^{18}O$ oxygen isotope effect of $\sim -10\%$. The observed isotope effects suggest the presence of Jahn-Teller polarons in these materials. [S0031-9007(96)01926-6]

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Recently, the ferromagnetic systems $La_{1-x}Me_xMnO_{3+y}$ (where Me = Ca,Sr,Ba) have become the focus of scientific and technological interest because of the colossal magnetoresistance (CMR) effects found in these materials [1]. Doped manganese perovskites are mixed-valent systems containing Mn^{3+} and Mn^{4+} ions. The magnetic and electronic properties in these compounds have traditionally been examined with the double exchange (DE) model, which considers the transfer of an electron between neighboring Mn^{3+} and Mn^{4+} ions through the Mn-O-Mn path [2]. The electron transfer depends on the relative alignment of the electron spin and localized Mn^{4+} spin. When the two spins are aligned, the carrier avoids the strong on-site Hund exchange energy and hops easily. Thus the DE model provides an explanation for a strong coupling between the charge carriers and the localized manganese moments. However, recent theoretical considerations indicated that DE alone does not explain the CMR, and that polaronic effects due to a very strong electron-phonon coupling should be included [3,4]. The strong electron-phonon coupling is expected because the electronic ground state of the Mn^{3+} ions is degenerate, and this degeneracy is removed by a spontaneous distortion of the surrounding lattice, known as the Jahn-Teller (JT) effect [5]. A recent demonstration of a giant oxygen isotope shift of >20 K on the ferromagnetic transition temperature T_c by Zhao *et al.* [6] provided direct experimental evidence of the strong coupling of the charge carriers to JT lattice distortions and of JT polaron formation [7] in $La_{1-x}Ca_xMnO_{3+y}$. In this Letter we report a study of oxygen isotope effects on the static and dynamic magnetic properties of $La_{1-x}Ca_xMnO_{3+y}$ by electron paramagnetic resonance (EPR). Significant differences of the EPR signal were observed in samples with different oxygen isotopes. Our results provide the first *microscopic* evidence for the formation of JT polarons [7] and for its relevance in determining magnetic properties of doped manganese perovskites.

The EPR measurements were performed at 9.4 GHz using a BRUKER ER-200D spectrometer. We measured the temperature dependence ($T_c < T < 3T_c$) of the EPR for ceramic powder samples of $La_{1-x}Ca_xMnO_{3+y}$ with $x = 0.1$, 0.2 which were substituted by different oxygen isotopes (^{16}O and ^{18}O). The samples used here are the same as those studied by Zhao *et al.* [6]. A strong symmetric EPR signal with a line shape very close to Lorentzian was observed over the whole range of temperatures investigated (except the region very near T_c, where some distortions of the line shape occur). Two typical EPR signals are shown in Fig. 1. In order to determine the temperature dependence of the EPR signals, we have fitted the spectra with a Lorentzian line shape (Fig. 1). The fitting parameters are the peak-to-peak linewidth ΔH_{pp} and the resonance field H_{res}. The resonance field corresponds to a g value of 2.0 and does not depend on temperature. The temperature dependence of the linewidth for the $x = 0.2$ sample with different oxygen isotopes is shown in Fig. 2. With decreasing temperature the linewidth decreases, passes through a minimum at a temperature T_{min}, and increases on further cooling to T_c. It is interesting that T_{min} in the ^{18}O sample is shifted to lower temperatures in comparison with the ^{16}O sample and that there are significant differences in linewidths below T_{min}. The integral intensity I of the EPR signal decreases with temperature much faster

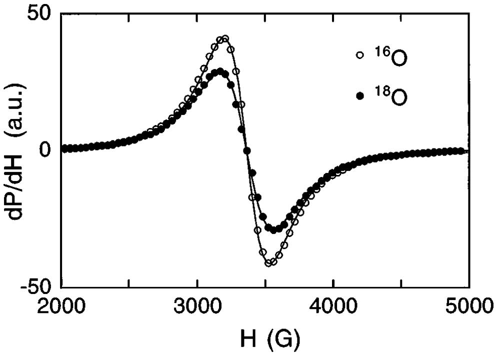

FIG. 1. An EPR signal of ^{16}O and ^{18}O samples of $La_{0.8}Ca_{0.2}MnO_{3+y}$ measured at $T = 300$ K under identical experimental conditions. The fits with Lorentzian line shape are indicated by solid lines.

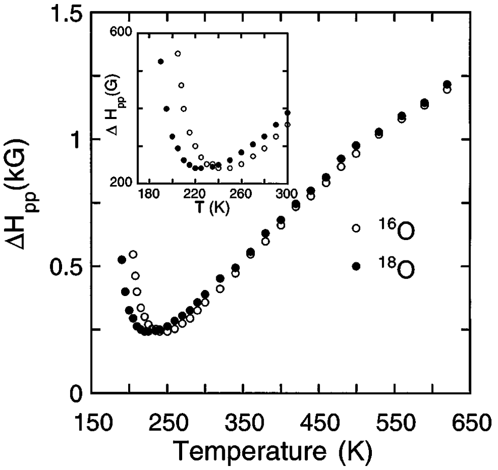

FIG. 2. Temperature dependence of the peak-to-peak EPR linewidth ΔH_{pp} for ^{16}O and ^{18}O samples of $La_{0.8}Ca_{0.2}MnO_{3+y}$. The inset shows the low temperature region on an enlarged scale.

than would be expected according to the Curie law. To show this, we plot in Fig. 3 the product $I \times T$ versus temperature. The multiplication by T eliminates the intrinsic temperature dependence of the EPR signal, caused by the Boltzmann population of the Zeeman levels involved. It is important to note that the EPR spectra for compounds with different oxygen isotopes were taken with exactly the same spectrometer conditions. Special care was also taken to measure the samples with the same mass, identical sample tubes, etc. The reproducibility of the measured EPR signals was checked several times. Thus the EPR signal intensity in samples with different oxygen isotopes can be directly compared. From Fig. 3, one can see that the intensity of the EPR signal in the ^{16}O sample is higher than in the ^{18}O sample.

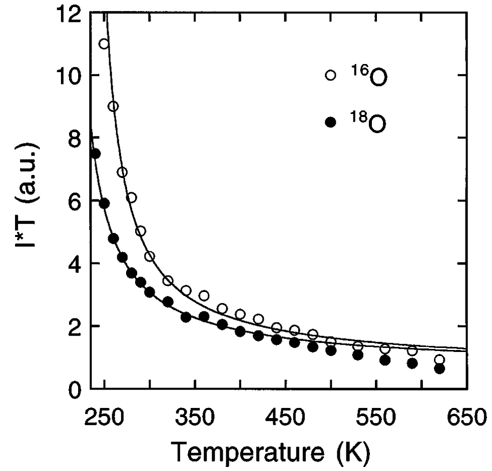

FIG. 3. Temperature dependence of the integral intensity of EPR signal times temperature ($I \times T$) for ^{16}O and ^{18}O samples of $La_{0.8}Ca_{0.2}MnO_{3+y}$. The solid lines represent the best fit to Eq. (1) in the temperature range $250 \leq T \leq 500$ K.

In order to understand the striking differences of resonance linewidths and intensities in different oxygen isotope samples, it is necessary to first clarify the origin of the EPR signal in manganese perovskites. Recently, Oseroff *et al.* [8] reported the first observation of an EPR signal in $La_{1-x}Ca_xMnO_{3+y}$ compounds with different Ca and oxygen content. They also observed strong EPR signals with an unconventional temperature dependence and suggested that a cooperative spin entity could be responsible for this signal. We propose that the EPR signal observed in $La_{1-x}Ca_xMnO_{3+y}$ is due primarily to Mn^{4+} ($3d^3$ with $S = 3/2$) ions. In an octahedral anion crystal electric field this ion has a ground state, corresponding to an orbital singlet A_2. Consequently the spin-lattice relaxation is weak, and this makes EPR of Mn^{4+} easy to observe even at high temperatures [9]. The Mn^{3+} ($3d^4$ with $S = 2$) is unlikely to have an observable EPR signal as it exhibits a large zero-field splitting and strong spin-lattice relaxation (the ground state of the Mn^{3+} ion is the orbital doublet) [10].

However, it is clear that the observed signal cannot be attributed to isolated Mn^{4+} ions. To construct a model of paramagnetic centers responsible for these EPR signals, it is important to point out that doped manganese perovskites are mixed valence compounds with Mn^{4+} and Mn^{3+} ions and strong ferromagnetic DE interaction between them. Thus, we should consider the EPR response of the system to contain three distinct components: Mn^{4+} ions, s; Mn^{3+} ions, σ; and the lattice, L. Figure 4 shows a standard schematic picture for such a system, with arrows indicating possible relaxation paths between components. The theory used to describe such a system was developed in connection with the EPR of localized magnetic moments in metals (see, for example, an excellent review by Barnes [11]). Later, Gulley and Jaccarino [12] applied this formalism to study the EPR of strongly exchange-coupled insulators with two types

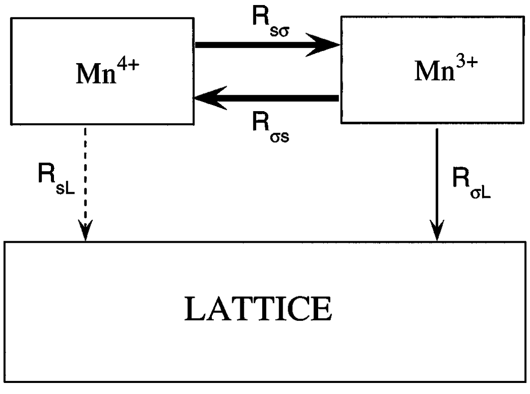

FIG. 4. A Block diagram showing the energy flow paths for the Mn^{4+} and Mn^{3+} spin subsystems and the lattice. The relaxation rate R_{ab} represents relaxation from subsystem a to subsystem b. The thickness of the arrows is a measure of the magnitude of the particular relaxation rate R_{ab}.

of paramagnetic ions. In order to describe the spin relaxation process in $La_{1-x}Ca_xMnO_{3+y}$ we consider the schematic block diagram shown in Fig. 4. Assuming that the relaxation rate $R_{\sigma L}$ of the Mn^{3+} spins to the lattice is much smaller than the exchange-induced cross relaxation rate $R_{\sigma s}$ (and back $R_{s\sigma}$) between Mn^{3+} and Mn^{4+}, and if the direct relaxation of Mn^{4+} ions to the lattice R_{sL} is negligible ($R_{\sigma L}, R_{sL} \ll R_{\sigma s}, R_{s\sigma}$), then a so-called "bottleneck" effect will take place in the transfer of energy between the spin subsystems [11]. In this limit, magnetic energy, which is transferred from the Mn^{4+} to the Mn^{3+} spin system, is quite likely to be returned back rather than passed on to the lattice. Consequently, the relaxation of the system is dominated by the bottleneck due to the slow Mn^{3+}-lattice relaxation process. Recently, the concept of a bottleneck was successfully applied by Kochelaev *et al.* [13] to explain the EPR of Mn ions in the cuprate superconductor $La_{2-x}Sr_xCuO_4$ in which antiferromagnetic coupling is present. This concept is also helpful in explaining the peculiar EPR features in $La_{1-x}Ca_xMnO_{3+y}$ and is our starting point for the interpretation of the experimental results.

Let us consider first the temperature dependence of the linewidth presented in Fig. 2. Below $T_{\min}$ the broadening is associated with a critical "slowing down" of the spin fluctuations in ferromagnets when T_c is approached from above [14]. Qualitatively, the critical slowing down arises from the growth of the correlation length ξ and of the lifetime of the critical magnetization fluctuations. This behavior is well known in ferromagnets and will not be discussed here. The mechanism of line broadening in the range $T > T_{\min}$ is different. It is caused by the spin-lattice relaxation. However, as was mentioned above, the spin-lattice relaxation for the Mn^{4+} is expected to be weak. It seems that the most relevant mechanism is one involving the exchange coupling of the Mn^{4+} to Mn^{3+} ions that quickly relax into the lattice. In the case when the spin-lattice coupling is considerably weaker than the exchange interaction between magnetic ions (bottleneck regime), the EPR linewidth is determined by the Mn^{3+} spin-lattice relaxation rate $R_{\sigma L}$ (Fig. 4) and increases with temperature [12].

It is also possible to explain why the EPR signal in $La_{1-x}Ca_xMnO_{3+y}$ is much stronger than what is expected from individual Mn^{4+} ions, as well as its sharp decrease with temperature above T_c. The intensity of the EPR signal is proportional to the static magnetic susceptibility of the ions responsible for the signal ($I \propto \chi_s$) [10]. In the bottleneck regime, χ_s is renormalized due to the exchange coupling [13]:

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

Here χ_s^0 and χ_σ^0 are the bare (without exchange) susceptibilities of the Mn^{4+} and Mn^{3+} ions, respectively. The factor λ is a dimensionless exchange coupling constant between them:

$$\lambda = \frac{zJ}{N g_s g_\sigma \mu_B^2} , \tag{2}$$

where z is the number of nearest neighbors, N is the total number of Mn spins per cm^3, and g_s and g_σ are the g factors of Mn^{4+} and Mn^{3+} ions, respectively. Equations (1) and (2) show that, in the present case of ferromagnetic coupling ($J > 0$), the intensity of the EPR signal is enhanced in comparison to that expected from individual Mn^{4+} ions. To show that these equations also describe correctly the temperature dependence of our EPR signal intensity, we analyzed the experimental results presented in Fig. 3 in terms of this model. We assumed that the bare susceptibility of Mn^{4+} ions follows the Curie law $\chi_s^0 = C_s/T$. For Mn^{3+} we used a Curie-Weiss law $C_\sigma/(T - \theta)$ with a negative Curie-Weiss temperature θ consistent with the antiferromagnetic interactions present in the $LaMnO_3$ parent compound [15]. The result of this fit using only a single free parameter, namely, the exchange integral J, is shown in Fig. 3. The agreement with the experimental data is fairly good below 500 K. The fit yields $J = 78(1)$ K for ^{16}O and $J = 71(1)$ K for ^{18}O. We are not aware of another experimental determination of the exchange integral between Mn^{4+} and Mn^{3+} ions in the paramagnetic regime of these compounds. However, a theoretical estimation by Eremin [16] in the presence of the JT effect gives a value of $J \simeq 30$ K. As can be seen from Fig. 3, above 500 K the intensity of the EPR signal drops faster than is predicted by Eq. (1). This deviation can be associated with a gradual transition from the bottleneck to the isothermal regime. In fact, the spin-lattice relaxation of Mn^{3+} ions $R_{\sigma L}$ is increasing with temperature and could become comparable to the exchange-induced cross relaxation $R_{\sigma s}$. In this case the bottleneck condition breaks down, and we have a transition to the isothermal regime, where Eq. (1) is no longer valid. In the isothermal regime ($R_{\sigma L} \gg R_{\sigma s}$) the broadening of the resonance line is limited by the finite probability of the exchange cross relaxation $R_{\sigma s}$, which is temperature independent [12]. As can be seen from Fig. 2, the EPR linewidth above 500 K shows a tendency to saturate, which confirms our assumption that above this temperature there is a transition from the bottleneck to the isothermal regime.

Before we consider the EPR response of samples with different oxygen isotopes (^{16}O and ^{18}O) in terms of our model for spin dynamics in $La_{1-x}Ca_xMnO_{3+y}$, let us summarize its main features. We assume that the spin system of the Mn^{4+} and Mn^{3+} ions displays a collective motion of their total magnetic moments (bottleneck regime), which is a consequence of a strong ferromagnetic coupling between them. The relaxation of these ions to the lattice is ineffective in destroying this collective mode, at least below 500 K. In terms of this model it is easy to explain the striking changes of the EPR linewidth and the intensity with oxygen isotope substitution if we assume that the exchange integral J is larger in ^{16}O samples than in ^{18}O samples. Indeed, according to Eq. (1), for ferromagnetic exchange ($J > 0$) a larger J corresponds to a higher EPR signal intensity (see Fig. 3). It is worthy to note that a fit to the data in Fig. 3 using Eq. (1) gives a value of J for the ^{16}O sample which is about 10% larger than for the ^{18}O sample. This difference in J should be compared with the 10% difference of T_c observed in these samples ($T_c \approx 207$ and 186 K for the ^{16}O and ^{18}O samples, respectively) [6]. The shift of $T_{\min}$ to lower temperatures in the ^{18}O sample (see Fig. 2) can also be easily understood. This sample has a lower T_c due to the smaller J, thus critical broadening starts at lower temperatures in comparison with the ^{16}O sample. Here we should note that, qualitatively, the same results were obtained for the $x = 0.1$ sample. The EPR linewidth and intensity also depend on the oxygen isotope mass, but the changes observed were slightly smaller then in the $x = 0.2$ sample, in accordance with the smaller oxygen isotope effect found for $x = 0.1$ [6].

The analysis of our results leads to the conclusion that the ferromagnetic exchange integral between Mn^{4+} and Mn^{3+} ions depends on the oxygen mass and $J(^{16}\mathrm{O}) > J(^{18}\mathrm{O})$. This important fact can be understood in terms of JT polaron formation in $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_{3+y}$, which was considered by Zhao *et al.* [6] to explain the giant oxygen isotope effect on T_c observed in this compound. In the JT polaron model the exchange integral J is proportional to the effective bandwidth W_{eff} of JT polarons, which, in turn, depends on the isotope mass [6],

$$W_{\mathrm{eff}} \propto W \exp(-\gamma E_{\mathrm{JT}}/\hbar\omega)\,, \tag{3}$$

where W is the bare conduction bandwidth, E_{JT} is the JT stabilization energy, and ω is the characteristic frequency of the optical phonons depending on the isotope mass M ($\omega \propto M^{-1/2}$). The dimensionless parameter γ is a function of E_{JT}/W with $0 < \gamma \leq 1$. According to Eq. (3), W_{eff} and, in turn, J decrease with enhanced oxygen isotope mass, in agreement with the present experimental observations.

In conclusion, we have observed an oxygen isotope effect on the EPR signal in $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_{3+y}$ with $x = 0.1$ and 0.2. We used a bottleneck model [13], which quantitatively explains the unusual EPR response in this compound, as well as its dependence on oxygen isotope mass. The present investigation shows that EPR can be a very effective tool to clarify complex magnetic interactions in doped manganese perovskites.

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