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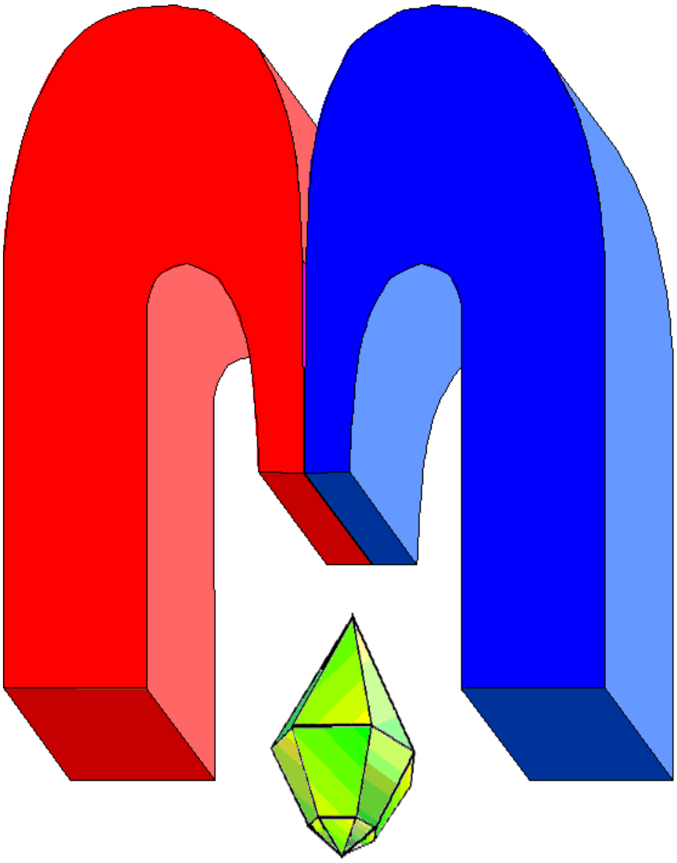

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[*] In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Spin relaxation of Mn ions in rare earth manganites in paramagnetic region[†]

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Role of bottlenecked spin relaxation and proportionality between small polaron hopping conductivity and electron paramagnetic resonance (EPR) linewidth (intensity) was emphasized. This idea gave a background for several experimental and theoretical investigations and it was starting point for its further generalization on variable range hopping conductivity and its influence on EPR linewidth in rare earth manganites.

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1. Introduction

Rare earth manganites with the common formula $A_yB_{1-y}MnO_3$ (where A = La, Sm, Pr or another rare-earth ion and B = Ca, Ba, Sr; $y = 1/3$) are members of a large series of rare-earth manganites exhibiting giant magnetoresistance. Their transport, magnetic and structural properties are very sensitive to the substitution of trivalent rare-earth ion (A^{3+}), as well as that of divalent ions (B^{2+}). These compounds have been the subjects of several investigations, including ferromagnetic resonance and electron paramagnetic resonance (EPR) investigations of Mn ions. Special attention was given to the spin dynamics of the Mn ions near the magnetic phase transition and explanation of pseudolinear increase in EPR linewidth in the paramagnetic state of these compounds above the Curie temperature. There are several explanations of this pseudolinear increase and one of most interesting and convincible theory was presented by group of investigators under guidance of Prof. B. Kochelaev in 2000 [1]. This outstanding paper gave new impact to understanding of the nature of the paramagnetic center responsible for the EPR signal and spin relaxation of paramagnetic centers in rare earth manganites.

In previous paper [2] a model was proposed 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. The existence of magnetic polarons was proved clearly in this paper. This model provides a reasonable explanation of the observed EPR signal as well as on the observed isotope effects. Further, the idea about the proportionality of hopping conductivity of e_g electrons and EPR linewidth along with bottlenecked regime of spin relaxation in manganites was brought up in this pioneer work [1]. This idea turned out very fruitful and led to several experimental and theoretical investigations. Therefore we have to remind main important points of this work.

2. Spin relaxation mechanism

2.1. *EPR linewidth*

The peak-to-peak first derivative EPR linewidth for $T > T_{\min}$, for the various manganite samples can be expressed as a sum of two terms, one of which is temperature independent, whereas the

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[†] This paper is originally written by authors on the occasion of eightieth birthday of Professor Boris I. Kochelaev.

other is temperature dependent, so that $\Delta B_{\mathrm{pp}} = \Delta B_{\mathrm{pp,\,min}} + \Delta B_{\mathrm{pp}}(T)$. The temperature-dependent EPR linewidth $\Delta B_{\mathrm{pp}}(T)$ is proportional to the magnetic susceptibility, and is given as [3, 4]:

$$\Delta B_{\mathrm{pp}}(T) = \frac{\chi_0(T)}{\chi(T)} \Delta B_{\mathrm{pp}}(\infty), \tag{1}$$

where $\chi_0(T) \propto T^{-1}$ is the free spin (Curie) susceptibility; χ is the measured susceptibility; and $\Delta B_{\mathrm{pp}}(\infty)$ is the temperature-independent value. Huber et al. [4] calculated the influence of exchange narrowing, using a general expression for the relaxation rate of the total spin. This approach is based on the memory function formalism developed by Mori [5], calculating $\Delta B_{\mathrm{pp}}(T)$ as a function of the second and fourth-order moments, M_2 and M_4, and concluding, that the main reason for broadening is the variation of the orthorhombic crystal-field parameters over the various Mn ions. The influence of the antisymmetric exchange interaction (Dzialozhinsky-Moriya) on EPR linewidth was found to be important [4]. However, the calculations showed very little influence of the dipole-dipole interactions in these manganite compounds, in agreement with the calculations of Huber et al. [3, 4].

2.2. Bottlenecked spin relaxation

Proportionality between the EPR linewidth and the conductivity is often observed in systems with hopping conductivity [6]. 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 [7]. 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 manganites is very close to 2. Therefore the condition for the bottleneck regime $W_s \ll W$ is satisfied.

2.3. Hopping conductivity

A linear relation between the EPR linewidth (ΔB_{pp}) and conductivity is often observed in systems exhibiting hopping conductivity. Rare earth manganites belong to such systems [8]. In this context, it is noted that the minimum of the EPR linewidth in manganite samples occurs at T_{min}, which is near T_C, above which it increases with increasing temperature. The temperature dependence of ΔB_{pp} above T_{min} is very similar to that of the electrical conductivity observed in manganites [9]. Accordingly, the following expression was used to fit the EPR linewidth [3]:

$$\Delta B_{\mathrm{pp}}(T) = \Delta B_{\mathrm{pp,\,min}} + \frac{A}{T} \exp\left(-E_a/k_{\mathrm{B}}T\right). \tag{2}$$

As stated above, increasing disorder in the distribution of Mn^{4+} and Mn^{2+} ions due to doping with Ba ions requires the application of variable-range-hopping (VRH) model for the charge-transfer process in manganites. Accordingly, the temperature dependence of conductivity can be expressed as [10]:

$$\sigma = \sigma_0 \exp\left(-(T_0/T)^{1/4}\right), \tag{3}$$

where T_0 is the characteristic temperature; its value for manganites is around 10^6 K [11]. Then the EPR linewidth can be similarly expressed as [12]:

$$\Delta B_{\mathrm{pp}}(T) = \Delta B_{\mathrm{pp,\,min}} + C \exp\left(-(T_0/T)^{1/4}\right). \tag{4}$$

In Eq. 4, $T_0 = 18/k_\mathrm{B}\xi^3 N(E_p)$, $N(E_p)$ is the density of states on the Fermi level; ξ is the localization length; it is of order of the distance between adjacent Mn ions.

3. The application of this theory to $(\mathrm{La}_{033}\mathrm{Sm}_{0.67})_{0.67}\mathrm{Sr}_{0.33-x}\mathrm{Ba}_x\mathrm{MnO}_3$

The well-known small-polaron hopping model for the interpretation of EPR linewidth in the paramagnetic region [1] was first used to explain the linewidth behavior. In this model influence of small-polaron hopping conductivity in the paramagnetic state in highly doped manganite samples $(\mathrm{La}_{033}\mathrm{Sm}_{0.67})_{0.67}\mathrm{Sr}_{0.33-x}\mathrm{Ba}_x\mathrm{MnO}_3$ (x = 0.0, 0.13, 0.23, 0.33) [13], accompanied by flip-flop of spins, during the transfer of electrons from Mn^{2+} to Mn^{3+}, is considered to lead to broadening of EPR linewidth, as it was explained above. The best-fit parameters in Eq. 2 are: $\Delta B_{\mathrm{pp,\,min}} = 33.4$, 50.5, 54.0, 64.8 mT, and $E_a = 0.26$, 0.089, 0.090, 0.089 eV for the samples with $x = 0.0$, 0.13, 0.23, 0.33, respectively. The activation energy E_σ was derived from temperature dependence of hopping conductivity in small polaron model. The conductivity data were fitted to temperature-dependent expression, similar to Eq. 2, obtaining the values $E_\sigma = 0.25$, 0.18, 0.18, 0.18 eV for the samples with $x = 0.0$, 0.13, 0.23, 0.33, respectively. A comparison of E_a and E_σ values determined here reveals that these two values are equal for the sample with $x = 0.0$ without Ba^{2+} ions, whereas the value of E_σ is about twice that of E_a for the samples with $x = 0.33$, 0.23, and 0.13, in which there is a partial replacement of Sr^{2+} ions by Ba^{2+} ions. Similar effect for replacement of Ca ions by Ba ions in rare earth manganites was observed by Ulyanov et al. [14, 15]. Therefore this difference, as well abrupt change in E_a, E_σ depending on x, needs to be explained.

There are many evidences for variable range hopping (VRH) conductivity of manganites [16] and, in particular, for $(\mathrm{La}_{1/3}\mathrm{Sm}_{2/3})_{2/3}\mathrm{Sr}_{1/3-x}\mathrm{Ba}_x\mathrm{MnO}_3$ samples [17]. Assuming that the EPR linewidth is proportional to the conductivity in $(\mathrm{La}_{1/3}\mathrm{Sm}_{2/3})_{2/3}\mathrm{Sr}_{1/3-x}\mathrm{Ba}_x\mathrm{MnO}_3$, whose behavior is governed by the VRH model, it is possible to describe both hopping conductivity and EPR linewidth in similar manner. Eq. (4) was used to evaluate the VRH parameter T_0. This parameter was estimated for the samples $(\mathrm{La}_{1/3}\mathrm{Sm}_{2/3})_{2/3}\mathrm{Sr}_{1/3-x}\mathrm{Ba}_x\mathrm{MnO}_3$ ($x = 0.0$, 0.01, 0.03, 0.06, and 0.13, 0.23, 0.33) from the dependence of EPR linewidth on temperature in the paramagnetic phase of these samples [12]. The decrease in T_0 with increasing Ba content is found to be quite sharp for the Ba-content $x = 0.0$ to 0.1, but this decrease is continuous in such approach. The best-fit parameter $T_0 = 1.64$, 0.59, 0.48, 0.14, 0.07, 0.04×10^6 for $x = 0$, 0.01, 0.03, 0.06, 0.13, 0.23. Therefore this explanation could be considered as successful for rare earth manganites under study.

It should be noted also, that there are also alternative explanations of pseudolinear increasing EPR linewidth, for example, due phonon modulation of Dzyaloshinskii-Moriya antisymmetric interaction between exchange-coupled manganese ions [18], however, the recent experiments clearly show importance of charge transport process and static magnetization for explanation of spin relaxation of manganese ions in rare earth manganites. Here, it should mentioned also the interpretation of EPR linewidth in lightly doped manganites, such as $\mathrm{La}_{0.95}\mathrm{Sr}_{0.05}\mathrm{MnO}_3$, which was fulfilled also with participation of Prof. B.I. Kochelaev [19, 20] and also brought new knowledge, specifically, about orbital order in manganites.

4. Conclusion

This outstanding work [1] gives many new ideas, becomes very significant and it was cited already more than hundred times. It enforced the investigators to many new experiments and, therefore, it brought next step in understanding of spin relaxation in rare earth manganites. In particular, it led to the generalization of this approach from small polaron hopping to variable range hopping. Finally, it was shown, that variable range hopping also could explain pseudolinear increase of EPR linewidth in paramagnetic region of rare earth manganites.

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