Microscopic State of Low Doped Manganites $La_{1-x}Sr_xMnO_3$ Probed by ESR

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The electron spin resonance (ESR) measurements were performed in single crystals of $La_{1-x}Sr_xMnO_3$ ($0.05 \leq x \leq 0.125$) in order to study the interplay of crystal field, Dzyaloshinsky–Moriya interaction, Jahn–Teller (JT) effect, and orbital order. The angular dependence of the ESR linewidth of an untwinned $La_{0.95}Sr_{0.05}MnO_3$ single crystal has been analyzed in the high-temperature approximation, which takes into account the microscopic geometry of the four nonequivalent Mn positions in the orthorhombic unit cell. A strong mixing of the $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ states for the real orbital configuration was found. Magnetic inhomogeneities observed in the ESR spectra across the composition range $0.075 \leq x \leq 0.125$ can be attributed to the presence of ferromagnetic clusters (magnetic spin polarons) in the paramagnetic state. New polaronic models are proposed.

1. INTRODUCTION

The perovskite manganites $La_{1-x}{}^{3+}Me^{2+}Mn_{1-x}{}^{3+}Mn_x{}^{4+}O_3$ (Me = Ca, Sr, Pb, and Ba) reveal a strong coupling of spin, charge, orbital, and lattice degrees of freedom. Fundamental for the physics of this system are the different spin states of Mn^{3+} and Mn^{4+}. The octahedral crystal field splits the five 3D (three-dimensional) orbitals into a lower triplet t_{2g} and an upper doublet e_g with an energy splitting of about 1 eV. In Mn^{4+} the three electrons occupy the lower t_{2g} triplet with parallel spin, yielding a spin $S = 3/2$, the upper e_g level is not affected. In contrast, in Mn^{3+} an additional electron occupies the upper e_g level with parallel spin due to strong Hund's-rule coupling, resulting in a spin $S = 2$. When occupied with a single electron, the orbitally degenerated e_g doublet is unstable against cooperative JT effect, which lifts the degeneracy, splits the e_g doublet by typically 0.1 eV, and leads to a strong orthorhombic (OR) distortion of the MnO_6 octahedra in the perovskite structure. We have studied the influence of crystal field (CF), Dzyaloshinsky–Moriya (DM) interaction, and JT effect on the ESR behavior of the low doped $La_{1-x}Sr_xMnO_3$ ($0.05 \leq x \leq 0.125$) single crystals within the OR distorted phase.

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2. EXPERIMENTAL DETAILS

The ESR experiments have been carried out with a Bruker ELEXSYS E500 CW-spectrometer at X- and Q-band frequencies ($\nu = 9.35$; 34 GHz). The measurements in the temperature range between 4.2 and 680 K were performed with continuous gas-flow cryostats for He (Oxford Instruments) and N_2 (Bruker). The full angular dependence of the ESR linewidth has been investigated for the untwinned small (volume = 2 mm^3) single crystal of $La_{0.95}Sr_{0.05}MnO_3$. The sample was fixed on a suprasil

quartz rod with low temperature glue (General Electrics) with respect to the orientation of the static magnetic field H in the three crystallographic planes (*ab*, *ac*, and *bc*). For other details and evaluation of the ESR spectra we refer to our previous publication [1].

3. RESULTS AND DISCUSSION

The spin Hamiltonian for a strongly exchange coupled magnetic system like $LaMnO_3$ can be written as $H = \boldsymbol{J} \sum_{(i<j)} S_i \cdot S_j - \beta \sum_i H \cdot \boldsymbol{g} \cdot S_i + H_{\text{int}}$. Here the first term describes the superexchange interaction between two nearest-neighbor Mn spins S_i and S_j with coupling constant $\boldsymbol{J}$. The second term is the Zeeman splitting of the spin states with gyromagnetic tensor $\boldsymbol{g}$ within an external magnetic field H, where β denotes the Bohr magneton. The third term H_{int} includes all interactions, which do not conserve the total spin and therefore contribute to the broadening of the ESR line as there are crystal field (CF), DM interaction, anisotropic exchange interaction, dipole–dipole interaction, hyperfine interaction. Because of estimation of their relative strength it turned out that CF and DM interaction yield by far the largest contributions [2]. In the case of strong exchange narrowing ($H_{\text{ex}} \gg H_{\text{int}}$), the ESR linewidth is determined by the second moment M_2 of the resonance line divided by the exchange frequency ω_{ex} [3]

$$\Delta H \cong M_2 (g\beta\hbar)^{-1} / \omega_{\text{ex}}. \qquad (1)$$

In the present case the second moment is caused by the sum of DM and CF contributions, which we have estimated very recently [4] using the structural data of the four nonequivalent Mn positions in the OR unit cell in $LaMnO_3$ obtained from neutron scattering measurements [5]. The absolute values of the CF parameters $D = 0.73(2)$ K and $E = -0.63(2)$ K are of nearly equal strength indicating comparable axial (D) and rhombic (E) distortions of the MnO_6 octahedra. The angular dependence of the resonance linewidth in $La_{0.95}Sr_{0.05}MnO_3$ at 200 K is well fitted with similar but slightly smaller parameters in Fig. 1. The fact that two CF parameters are of comparable strength is of particular importance for the picture of orbital order in $LaMnO_3$. In a local coordinate system the orbital of the e_g electron is a superposition $\psi_{g,e} = c_1\phi_{3z^2-r^2} \pm c_2\phi_{x^2-y^2}$ [6], where $c_1 = 0.8$ and $c_2 = 0.6$ denote the orbital mixing coefficients down to lowest temperatures on the base of neutron-diffraction studies [7].

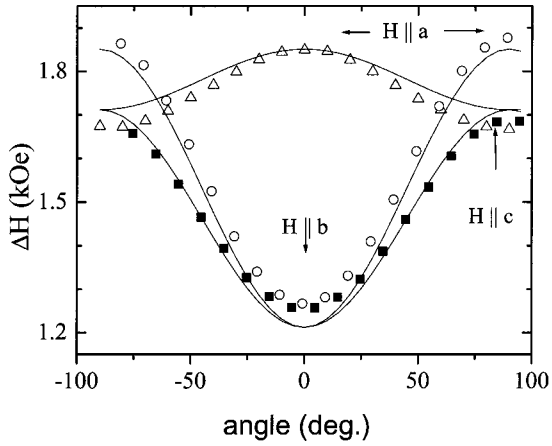

Fig. 1. Angular dependence of the ESR linewidth ΔH in $La_{0.95}Sr_{0.05}MnO_3$ for the magnetic field applied within the three crystallographic planes at 200 K. The solid lines represent the fit with Eq. (1).

Strong magnetic inhomogeneities that we have observed in the X-band ESR spectra of the Sr-doped manganites in the concentration range ($0.075 \leq x \leq 0.125$) [8] have been detected also in our Q-band measurements (Fig. 2). We think that these ESR data reveal the existence of the spin polarons and can contribute to identify their unknown nature. For example, an oxygen hole can be captured by the Mn^{4+}-ion (t_{2g}^3) because of its strong spin–spin coupling. The total spin of the corresponding $Mn^{4+}O_4^{7-}$ cluster is $S = 1$, and the angular dependence of the resonance field of the additional (to the main signal at $g \approx 2$) ESR lines at $T = 230$ K can be quite well fitted using the spin Hamiltonian

$$H = g\beta HS + D_1 S_z^2, \qquad (2)$$

where parameter $D_1 = 0.38$ K, $g_z = 1.76$, $g_x = 2.26$. Here x and z are aligned along a and c axis, respectively. However, as it shown in the Fig. 2, the spin polaron like Mn^{4+} can be also proposed for the description of this angular dependence in another possible model with $S = 3/2$, $D_1 = 0.19$ K, $g_z = 1.8$, $g_x = 1.97$.

In conclusion, the ESR experiments on the low doped Sr-manganites clarify the picture of orbital ordering and provide evidence about presence of magnetic spin polarons in the paramagnetic phase of these intriguing compounds.

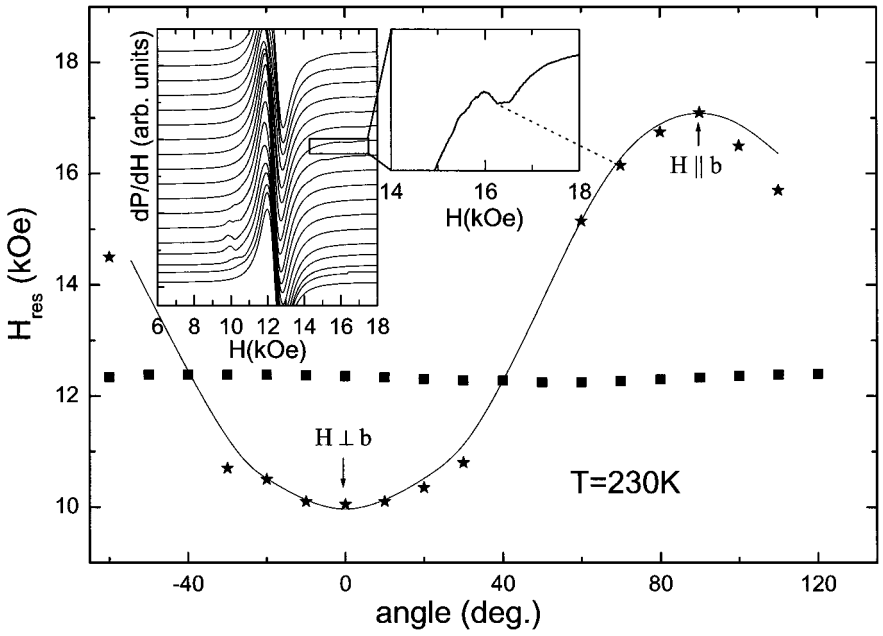

Fig. 2. Angular dependence of the resonance field $H_{\rm res}$ of the main ESR signal at $g \approx 2$ (solid squares) and the polaron signal (solid stars) in $La_{0.9}Sr_{0.1}MnO_3$ at 230 K. The crystallographic b axis was determined by model calculation, because the nearly cubic structure did not allow an identification from Laue experiments. Orientation transformations of the Q-band ESR spectra (at $\nu \approx 34.08$ GHz) are shown in the inset. The solid line describes the fit using the spin Hamiltonian (2) with $S = 3/2$, $D_1 = 0.19$ K, $g_z = 1.8$, $g_x = 1.97$.

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