Spin dynamics in $La_{2-x}Sr_xCuO_{4+\delta}$ doped with Mn as revealed by an ESR study

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(Received 17 December 1993)

The ESR, magnetic susceptibility, and resistivity measurements of $La_{2-x}Sr_xCuO_{4+\delta}$ doped with Mn are performed in the broad regions of temperature, Mn and Sr concentrations, respectively. The temperature and Mn concentration dependence of the ESR signal can be understood according to a model of the collective motion of the magnetic moments of Mn and Cu ions with the ESR linewidth determined mainly by the spin relaxation $\Gamma_{\sigma L}$ of the total magnetic moment of Cu ions to the lattice and by their susceptibilities (bottleneck effect). We found that $\Gamma_{\sigma L}$ is proportional to temperature $\Gamma_{\sigma L} \approx BT$ in a broad region of temperatures with B increasing with Sr doping. At low temperatures $T < T_{\min}$, with $T_{\min} \sim 20$–110 K depending both on Mn and Sr concentration, the ESR line experiences a sharp broadening which we attribute to the partial opening of the bottleneck. It reveals an inhomogeneous contribution to the Mn ESR linewidth and the relaxation rate $\Gamma_{s\sigma}$ of the Mn ions to the antiferromagnetic fluctuations in the CuO_2 layers, which were hidden in the bottleneck regime. We found $\Gamma_{s\sigma} \sim \Gamma^{\alpha}$, with $\alpha \approx 2$ for $T < T_{\min}$, and give some speculations on the origin of this broadening.

I. INTRODUCTION

Recently considerable efforts have been made to understand the low-frequency spin dynamics of the superconducting cuprates and the undoped parent compounds.[1–8] This activity is stimulated by the widespread belief that many aspects of this problem are closely connected with peculiar consequences of the two-dimensional spin correlations and fluctuations in CuO_2 layers and intimately related to the existence of high-T_c superconductivity itself. At the same time there is no consensus either on models of the spin dynamics in the normal and superconducting states or on the nature of high-T_c superconductivity. It seems therefore that new experimental results on the spin dynamics of Cu ions would be desirable. Since no direct electron-spin-resonance (ESR) signal from perfect CuO_2 planes has been observed (see, however, Ref. 9), the main information of the Cu spin dynamics comes from neutron scattering and nuclear-magnetic-resonance measurements (see Refs. 1–4, 10, and 11). It seems that most of these experiments provide information on the Cu spin system being in the thermal equilibrium state and leave not too many chances to observe the coherent relaxation rate of the Cu spins to the lattice.

In this paper we describe our ESR measurements of $La_{2-x}Sr_xCuO_{4+\delta}$ doped with Mn ions as an ESR probe and our model of the spin-relaxation process in this system. We believe that we are able to investigate the relaxation rate of a total magnetic moment of Cu ions to the lattice and its dependence on temperature and Sr concentration. Our measurements also give information which can be useful in comparing different approaches to the problem of the nature of spin correlations in CuO_2 layers of doped cuprates.

Our arguments for choosing the investigated system are the following: (a) the structure of the compound should be simple enough allowing for Cu to occupy only one site; (b) in order to create a disturbance of the Cu spin system the Larmor frequency of the ESR probe should be close enough to the precession frequency of the Cu ions; (c) the spin-bath relaxation of a probe should be ineffective to influence its coupling to the Cu spin system. It is evident that condition (a) suggests the La_2CuO_4 compound. To reduce possible channels of the spin-lattice relaxation of the probe, it is reasonable to choose the Mn^{2+} ion having a stable S-ground state. So conditions (b) and (c) are fulfilled almost automatically. Also it is important that Mn occupy the Cu sites in the CuO_2 planes.

In Sec. II we describe sample preparation, experimental procedure and results. In Sec. III we present our model of spin dynamics for CuO_2 layers with paramagnetic impurities, Sec. IV gives an interpretation of experimental results, and Sec. V concludes the article.

II. EXPERIMENT

A. Sample preparation

Mn-doped polycrystalline samples $La_{2-x}Sr_xCu_{1-y}Mn_yO_{4+\delta}$ with $0.0 \le x \le 0.3$ and $0.0 \le y \le 0.06$ were prepared by solid-state reaction from proper mixed powder of $SrCO_3$, La_2O_3, CuO, and MnO_2. A ground mixture of powder was heated in air at 1220 K for 5 h. Then the powders were annealed after cycles of regrinding in O_2 gas flow at 1420 K for 1 h. The powders were pressed into pellets and sintered at 1420 K for 50 h under O_2 gas flow, followed by cooling at the rate of 60 K/h down to 320 K. Finally, the pellets were again an-

nealed at 770 K for 50 h under O_2 gas flow.

The x-ray-diffraction analysis with the Cu $K\alpha$ at room temperature confirmed that the samples are crystallized in a single-phase tetragonal K_2NiF_4-type structure for $x \geq 0.1$. This corresponds to the composition dependence of the tetragonal-orthorhombic transition temperature of $La_{2-x}Sr_xCuO_{4+\delta}$ revealed by several authors.[12–14] The microprobe analysis was performed in order to control the quality of the samples. From Fig. 1 we can see that the samples are very homogeneous and compact. It is known that the loss of oxygen depends on the annealing program. To avoid different oxygen contents in our samples we exposed all samples with the same y simultaneously to a common annealing procedure.

For ESR investigation the pellets were ground again after the final annealing and the powder was suspended in paraffin. The grain sizes of the powder under investigation were around 10 μm and, therefore, less than the skin depth.

B. Electrical resistivity

We used a standard four-point method with lock-in technique to measure the resistivity as a function of temperature. The measuring current density was 0.1 A/cm^2 and the modulation frequency was set to 19 Hz. Temperature was detected by a germanium thermometer (below 32 K) and by a platinum thermometer (above).

As an example, Fig. 2 shows the temperature dependence of normalized resistivity observed in $La_{1.8}Sr_{0.2}Cu_{1-y}Mn_yO_{4+\delta}$ for different y values. Superconducting transitions (90–10%) were observed for $y=0$, 0.002, 0.01, and $y=0.02$ at $T_c=34$, 33, 24, and 8 K, respectively. These T_c values correspond to those of Xiao *et al.*[15] for Zn-doped samples. The doping with Mn^{2+} ions influences the superconductivity systematic and the value of T_c decreases rapidly with the Mn content (inset of Fig. 2). The solid curve in the inset of Fig. 2 is a fit of the relation $T_c=C(y_c-y)^{1/2}$ with $C=235$ K and $y_c=0.021$.[16,17] Due to the fact that this relation is a well established approximation only near y_c,[16] we tried also the linear relation for $T_c=T_c^0[1-0.69(y/y_c)]$,[17] which holds for $y\rightarrow 0$. In both cases we obtained almost the same fit parameter y_c. We estimate this good fit as a strong hint that the Mn ions substitute the Cu sites in the CuO_2 planes. Above T_c, for $y=0$, 0.002, and 0.01 the resistivity shows a positive temperature coefficient like a metal. For the 2% Mn sample $d\rho/dT$ changes sign at about 100 K and shows a behavior like a semiconductor at low temperature. The high-temperature slope of the resistivity decreases continuously with the Mn content for $T>150$ K.

FIG. 1. Microprobe photograph for polycrystalline $La_{1.8}Sr_{0.2}Cu_{0.98}Mn_{0.02}O_{4+\delta}$.

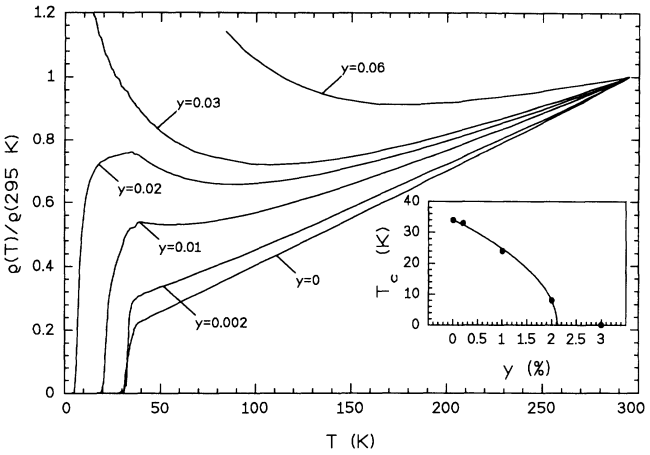

FIG. 2. The temperature dependence of normalized electrical resistivity $[\rho(T)/\rho(295\ \text{K})]$ in $La_{1.8}Sr_{0.2}Cu_{1-y}Mn_yO_{4+\delta}$ with different y. Inset shows the variation of T_c (90–10%) with Mn content and the solid line is a fit to the data using the relation (Refs. 16 and 17) $T_c=C(y_c-y)^{1/2}$ with $C=235$ K and $y_c=0.0211$.

C. ESR measurement

ESR experiments were performed on powdered samples using a standard Varian E-line spectrometer at an X-band frequency of about 9.3 GHz with 100-kHz field modulation. It is equipped with an Oxford Instruments helium-flow cryostat. The temperature was controlled between 4.2 and 300 K by an ITC-4 temperature controller of Oxford Instruments. The temperature at sample site above 20 K was detected by a platinum resistor.

In view of the spin dynamics in $La_{2-x}Sr_xCuO_{4+\delta}$, we doped Mn^{2+} ions into this system in order to probe the host Cu spin system by observing the ESR signal of Mn^{2+} ions. It is well known that Mn^{2+} ions are best suited to observe an ESR signal owing to their well-localized S-state character. We observed a definite signal with no fine and hyperfine structures in all temperature regions for all samples (Fig. 3). The resonance field at high temperature corresponds to $g\approx 2.0$. For samples which are superconductors, it was not possible to record the Mn^{2+} spectra for $T\leq T_c$ due to the very strong noise near the superconducting transition and the general broadening of the ESR lines at low temperatures.

In order to follow the temperature dependence of ESR linewidth, we have fitted the absorption derivative spec-

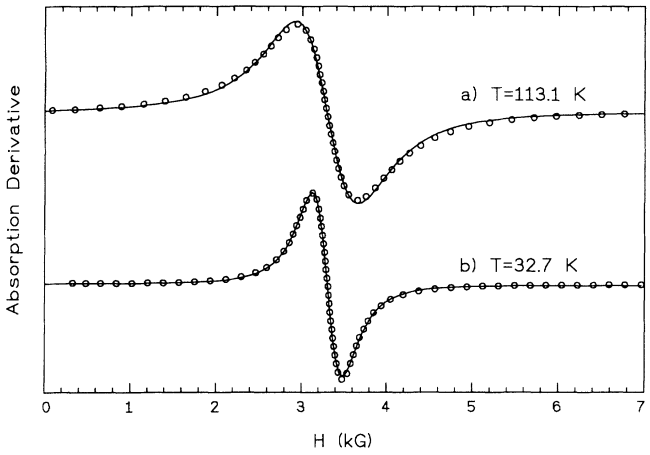

FIG. 3. A typical fit of powder spectrum of Mn^{2+} ESR in $La_{1.8}Sr_{0.2}Cu_{0.98}Mn_{0.02}O_{4+\delta}$ (circles) on the assumption of Lorentzian line shape (solid line).

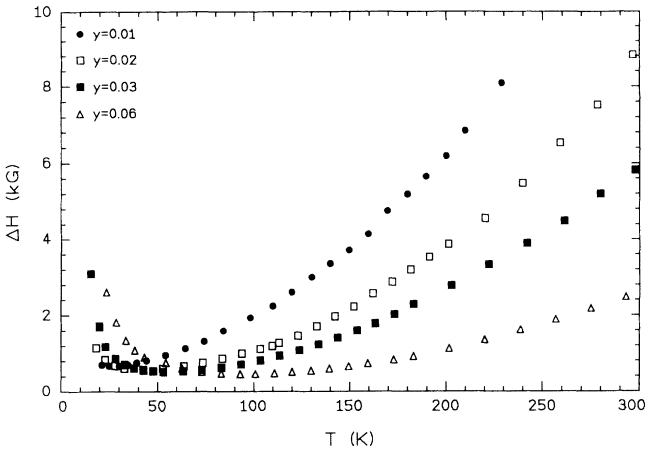

FIG. 5. Temperature dependence of Mn^{2+} ESR linewidth in $La_{1.8}Sr_{0.2}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.01$, 0.02, 0.03, and 0.06.

tra of the compound with the assumption of a Lorentzian line shape (Fig. 3). The substantial fit parameters are the linewidth ΔH and the resonance field H_{res}. Typical examples of the temperature dependence of the linewidth ΔH up to room temperature in the $La_{2-x}Sr_xCuO_{4+\delta}$ system are shown in Fig. 4. For $x=0$ the linewidth ΔH is more or less temperature independent between 100 K and room temperature typical for insulator behavior. For $x=0.1$, 0.2, and 0.3 the $La_{2-x}Sr_xCuO_{4+\delta}$ system is metallic and the linewidth ΔH decreases nonlinearly with decreasing temperature. It passes through a minimum and with further decreasing temperature it increases rapidly. Figure 5 shows the same behavior as a function of Mn content for $La_{1.8}Sr_{0.2}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.01$, 0.02, 0.03, and 0.06.

D. Magnetic susceptibility

The measurements of the magnetic susceptibility of the $La_{2-x}Sr_xCuO_{4+\delta}$ system were performed by using a dc superconducting quantum interference device magnetometer in the temperature range from 4.2 to 300 K. The measurements were performed at constant field $H_0=3.3$ kG. As an example, Fig. 6 shows the temperature dependence of the total reciprocal magnetic susceptibility of $La_{1.8}Sr_{0.2}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.01$, 0.02, 0.03, and 0.06. Note that if we try to fit the data by a Curie-Weiss law, the Curie constant is reduced to ~60% for all our samples compared with a typical Mn^{2+} value. A possible reason for this finding will be discussed below.

III. THE MODEL OF SPIN DYNAMICS

A. Preliminary discussion of the experimental results

The Mn^{2+} ion has a half-filled d-electron shell and is situated in the positions of Cu ions in the CuO_2 planes. The ground state of the d^5 configuration is determined by the relation between the crystal-field splitting and the spin coupling of electrons inside the ion. If the crystal field is not sufficient to outweigh this spin coupling, the

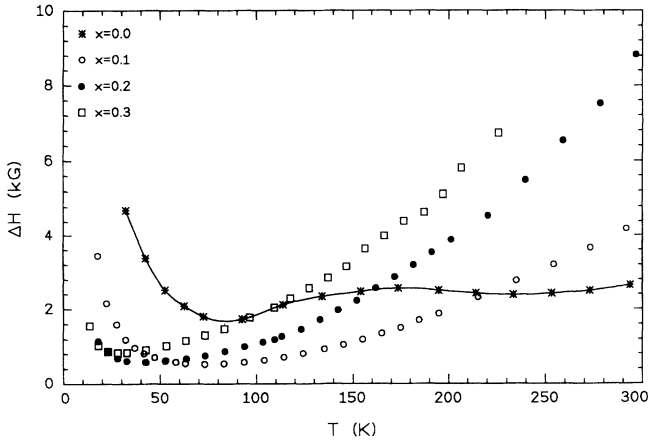

FIG. 4. Temperature dependence of Mn^{2+} ESR linewidth in $La_{2-x}Sr_xCu_{0.98}Mn_{0.02}O_{4+\delta}$ with $x=0$, 0.1, 0.2, and 0.3. The solid line is a guide for eyes.

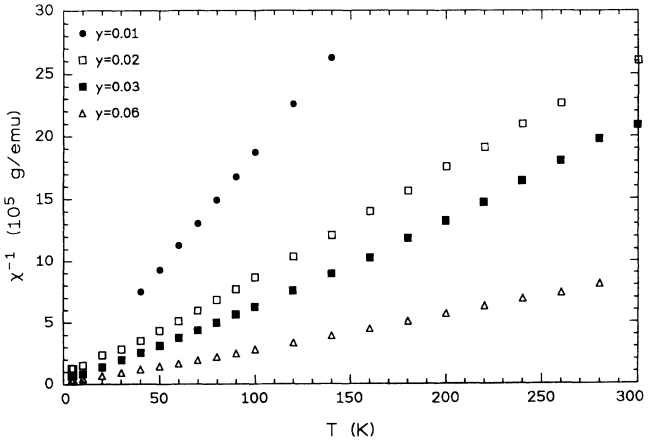

FIG. 6. Temperature dependence of the total reciprocal magnetic susceptibility for $La_{1.8}Sr_{0.2}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.01$, 0.02, 0.03, and 0.06. The measurements were performed at constant field $H_0=3.3$ kG.

ground state is an orbital singlet with $L=0$ and $S=\frac{5}{2}$, otherwise we have an orbital triplet with $S=\frac{1}{2}$. Our measurements of the static magnetic susceptibility show that although its experimental value is almost twice reduced in comparison with the usual Curie susceptibility for $S=\frac{5}{2}$, it seems there is no way to explain this value with $S=\frac{1}{2}$. In addition the orbital triplet would cause extra difficulties observing an isotropic ESR line. So we assume that we have the Mn^{2+} ion with the ground state ^6S.

The temperature dependence of the conductivity is typical for the $La_{2-x}Sr_xCuO_{4+\delta}$ system. The doping with Mn reduces both the conductivity in a normal state and the critical temperature T_c. We would like to call attention to the fact that the Mn concentration dependence of T_c is consistent with the Abrikosov-Gor'kov equation for the reduction of T_c by magnetic impurities derived for the low-T_c superconductors.

The main feature of the ESR results are the following: (a) observed was a single unresolved Lorentzian ESR line with a g factor $g_s \approx 2.0$; (b) the ESR linewidth increases nonlinearly with increasing T in temperature range $100 < T < 300$ K and with decreasing T at low temperatures having a minimum at 20–110 K, which depends both on Mn and Sr concentration; (c) the linewidth is strongly dependent on the Mn concentration being proportional to y^{-1} at high temperatures and increasing with y at low enough temperatures (Fig. 5); (d) the dependence on the Sr concentration of the ESR line is almost opposite to the y dependence (Fig. 4).

Points (a) and (c) bring to mind the features of the so-called "bottleneck effect" for ESR of localized moments which are coupled with conduction electrons by the isotropic exchange interaction (see, for example, an excellent review by Barnes[18]). In our case we can expect that Mn ions are relatively strongly coupled to the Cu spin system by the superexchange interaction. If the relaxation rate $\Gamma_{\sigma L}$ of the Cu spin system to other degrees of freedom (lattice, or generally "bath") is much less compared to the relaxation rate of Mn spins $\Gamma_{\sigma s}$ (and back $\Gamma_{s\sigma}$), and if direct relaxation of Mn ions to the lattice Γ_{sL} is ineffective, i.e., $\Gamma_{\sigma L}, \Gamma_{sL} \ll \Gamma_{\sigma s}, \Gamma_{s\sigma}$, then we can expect a situation similar to the bottleneck effect mentioned above. To the lattice, phonons and oxygen holes can be related (or holons and kinetic energy of spinons in the strong-coupling limit). This model of spin dynamics of high-T_c superconductors with paramagnetic impurities has been suggested already in Ref. 19 in order to understand the ESR of paramagnetic fragments of chains in YBaCuO compounds, coupled to the spin-system of CuO_2 planes.

In a phenomenological way the expected ESR linewidth and g factor for our system in a strong bottleneck regime can be written immediately in terms of introduced relaxation rates:[18]

$$\Delta H = \frac{1}{g_s\mu_B}\Gamma_{\text{eff}} = \frac{\chi_s^0\Gamma_{sL}+\chi_\sigma^0\Gamma_{\sigma L}}{g_s\mu_B(\chi_s+\chi_\sigma)} + \frac{\langle(\Delta\omega)^2\rangle}{g_s\mu_B\Gamma_{s\sigma}} , \quad (1a)$$

$$g_{\text{eff}} = \frac{\chi_s g_s + \chi_\sigma g_\sigma}{\chi_s+\chi_\sigma} . \quad (1b)$$

Here g_s and g_σ are the g factors of Mn and Cu ions, χ_s^0 and χ_σ^0 are the corresponding bare magnetic susceptibilities, while χ_s and χ_σ are renormalized ones by the mutual influence. The second term in (1a) represents the contribution of inhomogeneous broadening caused by the distribution of local fields, nonisotropic spin-spin interactions, and also by the fine and hyperfine structure, which is strongly reduced by the bottleneck narrowing process; $\langle(\Delta\omega)^2\rangle$ is the mean square of the bare shifts from resonance, producing inhomogeneous broadening.

The temperature and concentration dependence of the linewidth (1a) is consistent with observed features (a) to (d) at least at higher temperature, since one can expect an increase of relaxation rates $\Gamma_{\sigma L}$ and $\Gamma_{s\sigma}$ with temperature, and if we can neglect Γ_{sL} and take into account proportionality of the Mn ions spin susceptibility χ_s to their concentration y. It is likely to attribute an increase of the linewidth with increasing of Sr concentration at high temperatures to the opening of a new channel of relaxation of the spin system with doping of La_2CuO_4 by Sr.

In order to have explicit expressions for the relaxation rates we have to derive them for our system in a microscopical way.

B. Dynamical variables and interactions

To describe a response of the system of magnetic impurities in CuO_2 layers to a rf field we have to introduce according to our preliminary discussion at least two macroscopic dynamic variables,

$$\mathbf{M}_s = \langle \hat{\mathbf{M}}_s \rangle = g_s\mu_B \sum_{\mathbf{k}} \langle \hat{\mathbf{S}}_{\mathbf{k}} \rangle ,$$
$$\mathbf{M}_\sigma = \langle \hat{\mathbf{M}}_\sigma \rangle = \frac{1}{2} g_\sigma \mu_B \sum_{\mathbf{n}} \langle \hat{\boldsymbol{\sigma}}_{\mathbf{n}} \rangle . \quad (2)$$

Here $\hat{\mathbf{M}}_s$ and $\hat{\mathbf{M}}_\sigma$ are operators of the total magnetic moments of magnetic impurities and of the Cu ions, $\hat{\mathbf{S}}_{\mathbf{k}}$ and $\frac{1}{2}\hat{\boldsymbol{\sigma}}_{\mathbf{n}}$ are the corresponding spin operators for the impurity and the Cu ion at sites $\mathbf{k}$ and $\mathbf{n}$ in the CuO_2 plane; $\langle \cdots \rangle$ means an average with the nonequilibrium statistical operator. We have neglected the anisotropy of g factors, but a generalization for axial symmetry is straightforward.

The coupling between $\mathbf{M}_s$ and $\mathbf{M}_\sigma$ can be attributed mainly to the isotropic exchange interactions between magnetic impurities and the neighboring Cu ions

$$\mathcal{H}_{s\sigma} = -J_{s\sigma} \sum_{\mathbf{k},\delta} \hat{\mathbf{S}}_{\mathbf{k}} \hat{\boldsymbol{\sigma}}_{\mathbf{k}+\delta} , \quad (3a)$$

where $J_{s\sigma}$ is the exchange integral and the vectors δ connect the site $\mathbf{k}$ to its neighboring Cu sites $\mathbf{k}+\delta$. Regarding the symmetry of the La_2CuO_4 system, one can expect the existence of anisotropic correction to this interaction

$$\Delta\mathcal{H}_{s\sigma} = -\Delta J^z_{s\sigma} \sum_{\mathbf{k},\delta} \hat{\mathbf{S}}^z_{\mathbf{k}} \hat{\boldsymbol{\sigma}}^z_{\mathbf{k}+\delta} , \quad (3b)$$

where z components of vectors mean the projection on the c axis of the crystal; possible consequences of this term will be discussed later on.

Uniform precession of the magnetic moments $\mathbf{M}_s$ and

$\mathbf{M}_\sigma$ is controlled by the Zeeman Hamiltonians:

$$\mathcal{H}_{Zs}=-g_s\mu_B\sum_{\mathbf{k}}\mathbf{H}_0\hat{\mathbf{S}}_{\mathbf{k}}\ ,$$
$$\mathcal{H}_{Z\sigma}=-\frac{1}{2}g_\sigma\mu_B\sum_{\mathbf{n}}\mathbf{H}_0\hat{\boldsymbol{\sigma}}_{\mathbf{n}}\ , \tag{4}$$

where $\mathbf{H}_0$ is the external constant magnetic field. The ESR spectrum of impurities can be also affected by the crystal field and the hyperfine interactions, but since these interactions are much less in comparison to $J_{s\sigma}$, we can expect that they give only a small contribution to the ESR linewidth and we do not write them here explicitly. The same can be assumed for the dipole-dipole interactions. As a mater of fact all this sources of broadening of the line will be accumulated in the second term of (1a).

The following exchange interactions are responsible for the antiferromagnetic spin-spin correlations between Cu ions:

$$\mathcal{H}_0=\tfrac{1}{8}J_0\sum_{\mathbf{k},\delta}\hat{\boldsymbol{\sigma}}_{\mathbf{k}}\hat{\boldsymbol{\sigma}}_{k+\delta}\ , \tag{5}$$

A stationary ESR exists only if there is an interaction of the spin system with the bath (lattice), including phonons, electronic quasiparticles, and, as a consequence of the strong antiferromagnetic exchange interactions between the Cu ions, the two-dimensional spin fluctuations. As usual in metals we expect that the phonons play no significant role in the spin relaxation under consideration. The coupling of the Cu spins to the other degrees of freedom can be written quite generally in the form

$$\mathcal{H}_{\sigma L}=J_{\sigma L}\sum_{\mathbf{n}}\hat{\boldsymbol{\sigma}}_{\mathbf{n}}\hat{\mathbf{L}}_{\mathbf{n}}\ , \tag{6}$$

since any one-particle operator for the spin $S=\frac{1}{2}$ is linear in Pauli matrices. Here the operator $\hat{\mathbf{L}}_{\mathbf{n}}$ is independent on the Cu spins, and $J_{\sigma L}$ is the corresponding coupling constant. The Hamiltonian (6) is responsible for the relaxation of the Cu magnetic moment $\mathbf{M}_\sigma$ to the quasiparticles, since the commutator of the operator $\hat{\mathbf{M}}_\sigma$ with the isotropic exchange interactions between the Cu ions (5) equals zero and therefore antiferromagnetic fluctuations do not contribute directly to this relaxation rate. The interaction of magnetic impurities with quasiparticles can be written in a similar form.

Next we discuss briefly the value of coupling constants that appeared above. We expect that in Sr-doped samples the main channel of relaxation of the Cu spin system to the lattice opens due to appearance of holes in the oxygen p orbitals. In the weak-coupling limit (6) is nothing else but an exchange interaction between Cu ions and holes resulting in the usual Korringa relaxation. The corresponding exchange integral $J_{\sigma L}$ has contributions determined by the hopping integral t_0 between the $d_{x^2-y^2}$ and p_σ orbitals as well as due to their direct overlapping J_{dp}:

$$J_{\sigma L}=t_0^2\left[\frac{1}{\Delta}+\frac{1}{U-\Delta}\right]+J_{dp}\ , \tag{7}$$

where Δ is the one-hole energy and U is the on-site Coulomb energy of d orbitals. It is important to note that the second term in (7) J_{dp} is negative (ferromagnetic) because of its direct overlapping origin, which results in a reduction of the coupling constant under consideration. An estimation by Yeremin gives $J_{dp}=-0.5$ eV.[20] For the particular choice of parameters $t_0=1.3$ eV, $\Delta=3.5$ eV, $U=8.8$ eV,[21] we have finally $J_{\sigma L}=0.3$ eV. In the case of Mn one can expect that both t_0 and J_{dp} should be the same since the same orbitals are involved, but Δ and U are almost twice as large because of a more stable S-state configuration (Ref. 22). If we take $U-\Delta\approx\Delta=7$ eV, then the exchange integral between Mn ions and oxygen holes is almost canceled: $J_{SL}=-0.02$ eV. Of course, we should not take this estimation too seriously, but it can certainly indicate that $|J_{SL}|<|J_{\sigma L}|$ or even $|J_{SL}|\ll|J_{\sigma L}|$.

The superexchange antiferromagnetic interaction between neighboring Cu ions appears only in fourth order of perturbation theory in t_0, but we accept here the experimental value $J_0=1500$ K (≈0.13 eV). The corresponding superexchange interaction between Mn and Cu ions according to our previous consideration should be somewhat four times less and we take $2|J_{s\sigma}|=400$ K (we have to keep in mind the relation between Pauli and spin operators of Cu ions: $\hat{\boldsymbol{\sigma}}=2\hat{\mathbf{s}}$).

C. Equations of motion

Linearized equations for the total transverse magnetizations $M_s^{\mp}=M_{sx}\mp iM_{sy}$ and $M_\sigma^{\mp}=M_{\sigma x}\mp iM_{\sigma y}$ can be written similar to the Bloch-Hasegawa equations describing the ESR of magnetic impurities and conduction electrons.[18] Microscopic derivation of these equations can be made following Fazleyev[22] by means of the Zubarev nonequilibrium statistical operator. After the Fourier transform in time we have

$$\begin{aligned}-i\omega M_s^-(\omega)&=[-i\omega_s^*-\Sigma_{s\sigma}(\omega)-\Sigma_{sL}(\omega)]\delta M_s^-(\omega)\\&\quad+\frac{g_s}{g_\sigma}\Sigma_{\sigma s}(\omega)\delta M_\sigma^-(\omega)\ ,\\-i\omega M_\sigma^-(\omega)&=[-i\omega_\sigma^*-\Sigma_{\sigma s}(\omega)-\Sigma_{\sigma L}(\omega)]\delta M_\sigma^-(\omega)\\&\quad+\frac{g_\sigma}{g_s}\Sigma_{s\sigma}(\omega)\delta M_s^-(\omega)\ ,\end{aligned} \tag{8}$$

where

$$\omega_i^*=\omega_i\frac{1+\lambda\chi_j^0}{1-\lambda^2\chi_i^0\chi_j^0}\ ,\quad \omega_i=\frac{g_i\mu_BH_0}{\hbar}\ ,\quad i;j=s,\sigma;\sigma,s\ ,$$
$$\lambda=\frac{2zJ_{s\sigma}}{Ng_sg_\sigma\mu_B^2}\ . \tag{8a}$$

Here z is the number of the neighboring Cu ions of impurities, χ_s^0 and χ_σ^0 are the bare static magnetic susceptibilities of the magnetic impurities and the Cu ions, N is the number of Cu sites per cm^3. δM_i^- is the deviation of the corresponding magnetic moments from its value in the instantaneous internal field: $\delta M_i^-=M_i^--\chi_i^0[h_{\mathrm{rf}}^-+\lambda M_j^-]$, where h_{rf}^- is the transverse alternating magnet-

ic field. The real parts of the kinetic coefficients $\Sigma_{ij}(\omega)$ define the relaxation rates $\Gamma_{ij}(\omega)$ of the coupled motion of magnetic moments of impurities and the Cu ions:

$$\Gamma_{s\sigma}(\omega)=\mathrm{Re}\Sigma_{s\sigma}(\omega)=\frac{1}{2}\left[\frac{J_{s\sigma}}{\hbar}\right]^2\frac{1}{N_{\mathrm{pl}}}\times\sum_{\mathbf{q}}f_s(\mathbf{q})[K_\sigma^{zz}(\mathbf{q},\omega-\omega_s^*)+\tfrac{1}{2}K_\sigma^{\mp}(\mathbf{q},\omega)]\ , \tag{9a}$$

where $\mathbf{q}$ is running over the full Brillouin zone (BZ) of the square lattice and $N_{\mathrm{pl}}=Nc$ is the number of Cu ions in the plane CuO_2 with c as the distance between the planes. Here $K_\sigma^{zz}(\mathbf{q},\omega)$ and $K_\sigma^{\pm}(\mathbf{q},\omega)$ are the spectral densities of the Cu ions spin correlation functions:

$$K_\sigma^{zz}(\mathbf{q},\omega)=\int_{-\infty}^{+\infty}dt\sum_{\mathbf{n}}e^{-i\omega t+i\mathbf{qn}}\langle\sigma_0^z(0)\sigma_{\mathbf{n}}^z(t)\rangle_0\ ,$$
$$K_\sigma^{\mp}(\mathbf{q},\omega)=\int_{-\infty}^{+\infty}dt\sum_{\mathbf{n}}e^{-i\omega t+i\mathbf{qn}}\langle\sigma_0^-(0)\sigma_{\mathbf{n}}^+(t)\rangle_0\ , \tag{9b}$$

and $f_s(\mathbf{q})$ is the form factor for Mn ions:

$$f_s(\mathbf{q})=4(\cos q_x a+\cos q_y a)^2$$

with a as the lattice constant of the CuO_2 plane. Expression (9a) has been found in the usual high-temperature approximation $\hbar\omega_s,\hbar\omega_\sigma\ll k_BT$, and $\langle\cdots\rangle_0$ means the averaging with the equilibrium statistical operator. As a matter of fact spectral densities $K_\sigma^{zz}(\mathbf{q},\omega)$ and $K_\sigma^{\pm}(\mathbf{q},\omega)$ are closely related to the imaginary part of the dynamical spin susceptibility tensor $\chi_\sigma^{ij}(\mathbf{q},\omega)$ of Cu ions and to the isotropic "dynamic structure factor" $S(\mathbf{q},\omega)$, used in the theory of the two-dimensional quantum Heisenberg antiferromagnet[23,24] and in the theory of nuclear relaxation in La_2CuO_4:[4]

$$\tfrac{1}{4}K_\sigma^{jj}(\mathbf{q},\omega)=\frac{2\,\mathrm{Im}\chi_\sigma^{jj}(\mathbf{q},\omega)}{1-e^{-\beta\hbar\omega}}=S^{jj}(\mathbf{q},\omega)\ ,$$
$$S(\mathbf{q},\omega)=\sum_j S^{jj}(\mathbf{q},\omega)\ ,\quad\text{with } j=x,y,z\ \text{ and }\beta=k_BT\ . \tag{9c}$$

According to (10) the relaxation rate $\Gamma_{s\sigma}$ for $k_BT\gg\hbar\omega$ is proportional to longitudinal and transverse components of the dynamical spin susceptibility of Cu ions somewhat similar to the nuclear relaxation rate but for other frequencies:

$$\Gamma_{s\sigma}=\left[\frac{2J_{s\sigma}}{\hbar}\right]^2\frac{k_BT}{N_{\mathrm{pl}}}\sum_{\mathbf{q}}f_s(\mathbf{q})\,\mathrm{Im}\left\{\frac{\chi_\sigma^{\parallel}(\mathbf{q},\omega-\omega_s^*)}{\omega-\omega_s^*}+\frac{\chi_\sigma^{\perp}(\mathbf{q},\omega)}{\omega}\right\}. \tag{10}$$

The relaxation rates $\Gamma_{s\sigma}(\omega)$ and $\Gamma_{\sigma s}(\omega)$ satisfy the detailed balance equations

$$\frac{\chi_s^0\Gamma_{s\sigma}(\omega)}{g_s^2}=\frac{\chi_\sigma^0\Gamma_{\sigma s}(\omega)}{g_\sigma^2}\ . \tag{11}$$

The imaginary parts of $\Sigma_{ij}(\omega)$ define the second-order frequency shifts. The relaxation rates to the lattice $\Gamma_{sL}(\omega)$ and $\Gamma_{\sigma L}(\omega)$ have a similar form to (9a) [the form factor $f(\mathbf{q})=1$, if the interaction is local]:

$$\Gamma_{iL}(\omega)=\mathrm{Re}\Sigma_{iL}(\omega)=\frac{1}{2}\left[\frac{J_{iL}}{\hbar}\right]^2\frac{1}{N_{\mathrm{pl}}}\times\sum_{\mathbf{q}}[K_L^{zz}(\mathbf{q},\omega-\omega_i^*)+\tfrac{1}{2}K_L^{\mp}(\mathbf{q},\omega)]\ , \tag{12a}$$

where $i=s,\sigma$ and

$$K_L^{zz}(\mathbf{q},\omega)=\int_{-\infty}^{+\infty}dt\sum_{\mathbf{n}}e^{-i\omega t+i\mathbf{qn}}\langle L_0^z(0)L_{\mathbf{n}}^z(t)\rangle_0\ ,$$
$$K_L^{\mp}(\mathbf{q},\omega)=\int_{-\infty}^{+\infty}dt\sum_{\mathbf{n}}e^{-i\omega t+i\mathbf{qn}}\langle L_0^-(0)L_{\mathbf{n}}^+(t)\rangle_0\ . \tag{12b}$$

Similarly to (10) the relaxation rates Γ_{iL} are proportional to the dynamical spin susceptibility of the lattice (i.e., other degrees of freedom besides the total magnetic moments of Mn and Cu ions).

Solutions of equations of the type (8) are well known,[18] and we quote here only two extreme cases. In the strong bottleneck regime, which is defined by the condition for the relaxation rates

$$|\Gamma_{s\sigma}+\Gamma_{\sigma s}+i(\lambda\chi_s\omega_\sigma+\lambda\chi_\sigma\omega_s)|\gg|\Gamma_{\sigma L}-\Gamma_{sL}+i(\omega_\sigma-\omega_s)|\ , \tag{13}$$

where χ_s and χ_σ are effective spin susceptibilities

$$\chi_s=\chi_s^0\frac{1+\lambda\chi_\sigma^0}{1-\lambda^2\chi_\sigma^0\chi_s^0}\ ,\quad\chi_\sigma=\chi_\sigma^0\frac{1+\lambda\chi_s^0}{1-\lambda^2\chi_\sigma^0\chi_s^0}\ , \tag{14}$$

the observed ESR signal corresponds to the collective motion of $\mathbf{M}_s$ and $\mathbf{M}_\sigma$ and its linewidth and resonant frequency are determined by the following simple formulas:

$$\Gamma_{\mathrm{eff}}\cong\frac{\chi_s^0\Gamma_{sL}+\chi_\sigma^0\Gamma_{\sigma L}}{\chi_s+\chi_\sigma} \tag{15a}$$

and

$$g_{\mathrm{eff}}=\frac{\chi_sg_s+\chi_\sigma g_\sigma}{\chi_s+\chi_\sigma}\ . \tag{15b}$$

We would like to point out here once again that the described bottleneck regime is similar to the well known in metals, but the usual role of conduction electrons play in our case the almost localized Cu ions, while the present conduction electrons and holes are considered in the equilibrium state being a part of the lattice. An important feature of expression (15a) is that Γ_{eff} is strongly dependent on the concentration of impurities y if $\chi_s>\chi_\sigma$ and $\Gamma_{\sigma L}\gg\Gamma_{sL}$, since the spin susceptibility of impurities is proportional to y:

$$\chi_s^0=yNS(S+1)(g_s\mu_B)^2\frac{1}{3k_BT}\ . \tag{16}$$

When the ESR line of impurities experiences an additional inhomogeneous broadening mentioned in Sec. III A, there is an additional contribution to the linewidth

which is strongly reduced by the bottleneck narrowing process,[18]

$$\Delta\Gamma_{\rm eff}\cong {\rm Re}\frac{\langle(\Delta\omega)^2\rangle}{\Gamma_{s\sigma}+i\lambda\chi_\sigma\omega_s}\ , \tag{15c}$$

which is reduced to the second term of (1a) in the relaxation-dominated bottleneck regime.

If the inequality (13) is reversed and still $\omega_s\sim\omega_\sigma$, we have the isothermal regime and the effective ESR linewidth of impurities is determined by

$$\Gamma_{\rm eff}^{\rm isoth}=(\Gamma_{s\sigma}+\Gamma_{sL})\left[1-\frac{\theta}{T}\right]\ , \tag{17a}$$

where θ is defined by

$$\frac{\theta}{T}=\lambda^2\chi_\sigma^0\chi_s^0\ ; \tag{17b}$$

it is easy to see that $\Gamma_{\rm eff}^{\rm isoth}$ is almost independent of y at $T\gg\theta$.

D. Relaxation rates

The key question, what kind of spin dynamics can we expect in the system under consideration, depends on the relation between relaxation rates entering in the inequality (13). At first we consider an efficiency of the coupling between the spin system of impurities and Cu ions, which is controlled by the relaxation rates $\Gamma_{s\sigma}(\omega)$ and $\Gamma_{\sigma s}(\omega)$. All the properties of these relaxation rates according to Eqs. (9a)–(9c) are entirely determined by the imaginary part of the dynamical spin susceptibility of the Cu spin system similar to nuclear relaxation rates. Now there is probably not too much doubt that the strong antiferromagnetic correlations of the nearly localized Cu^{2+} d orbitals play an important role in the understanding of the novel properties of the cuprate oxides both in the insulating and metallic states. At the same time there are different approaches to the derivation of the properties of the mentioned correlation function including as the starting points, on the one hand the Fermi-liquid theory,[1–3,25] and on the other hand the theory of a two-dimensional quantum Heisenberg antiferromagnet (QHAF).[23,24]

In order to estimate the relaxation rate $\Gamma_{s\sigma}$ we use both of these approaches. According to the phenomenological theory of the antiferromagnetic Fermi liquid[1–3,25] (AFFL) the dynamical structure factor $S(\mathbf{q},\omega)$ has the form

$$S(\mathbf{q},\omega)=\frac{k_BT}{\hbar\omega}\,{\rm Im}\frac{\chi_{\mathbf{Q}}}{1-\xi^2(\mathbf{q}-\mathbf{Q})^2-i\omega/\omega_{\rm SF}}\ ,$$
$$\omega_{\rm SF}=\frac{E}{\beta^{1/2}\pi(\xi/a)^2}\ ,\quad \chi_{\mathbf{Q}}=\chi_0\left[\frac{\xi}{a}\right]\beta^{1/2}\ ,\quad q_x>0,q_y>0\ , \tag{18}$$

where $E\approx0.4$ eV plays the role of a magnetic Fermi energy (in Refs. 1–3, $E\equiv\Gamma$), χ_0 is the long-wave length static spin susceptibility, ξ is the spin-correlation length, $\mathbf{Q}=(\pi/a,\pi/a)$, and $\beta\approx\pi^2$. Having in mind that ω_s and ω_σ are small compared to the important frequencies of antiferromagnetic fluctuations in the considered temperature region and that in the disordered phase the correlation function is isotropic, we can put in Eqs. (9a) and (10), $\omega-\omega_s^*\approx\omega=0$, and $K_\sigma^{zz}=\frac{1}{2}K_\sigma^{\mp}$. The main contribution in the averaging of the dynamical structure factor in $\mathbf{q}$ space comes from the region close to the wave vector $\mathbf{Q}=(\pi/a,\pi/a)$ and using the result of this averaging from Ref. 3 we have

$$\Gamma_{s\sigma}({\rm AFFL})=\frac{5.3\pi}{\hbar}\left[\frac{J_{s\sigma}^2}{E}\right]\left[\frac{\xi}{a}\right]^2\frac{\chi_0}{(g_\sigma\mu_B)^2}k_BT$$
$$=\gamma_{\rm AFFL}(\xi)\cdot T\ . \tag{19}$$

To get some idea of the order of magnitude of $\Gamma_{s\sigma}({\rm AFFL})$ we take the value $|J_{s\sigma}|\sim200$ K according to our estimation in Sec. III B, and $\chi_0/(g_\sigma\mu_B)^2\sim2$ $({\rm eV})^{-1}$,[2] which leads to $\Gamma_{s\sigma}({\rm AFFL})\sim1.6\times(\xi/a)^2\times10^{11}$ sec^{-1} at 50 K.

Next we calculate $\Gamma_{s\sigma}$ using the dynamical structure factor found in the QHAF theory.[23,24] Averaging of this $S(\mathbf{q},\omega)$ has been performed in Ref. 6, which gives for $\Gamma_{s\sigma}$ in (9a)

$$\Gamma_{s\sigma}({\rm QHAF})=\frac{14.8\sqrt{\pi}}{Z_c\hbar}\left[\frac{J_{s\sigma}^2}{J_0}\right]\left[\frac{\xi}{a}\right]\left[\frac{k_BT}{2\pi\rho_s}\right]^{3/2}$$
$$\times\left[\frac{1}{1+T/2\pi\rho_s}\right]^2=\gamma_{\rm QHAF}(\xi)\cdot T^{3/2}\ , \tag{20}$$

where J_0 is the exchange integral between the Cu ions, ρ_s is the zero-temperature spin stiffness ($\approx0.15J_0$) and $Z_c\approx1$. Taking again $|J_{s\sigma}|\sim200$ K and $J_0\sim1500$ K, we have $0.57\times10^{12}\times(\xi/a)$ sec^{-1}.

According to QHAF theory the correlation length ξ increases exponentially with $1/T$, and AFFL theory suggests $\xi^2\sim1/(T+T^*)$. At the same time we cannot expect that in the Sr-doped cuprates ξ would increase to infinity, and it seems that only relatively short-wave correlations are responsible for the relaxation rate $\Gamma_{s\sigma}$ in this case. Since at the distances less than ξ antiferromagnetic spin waves are well defined even in the paramagnetic phase,[4,23,24] it becomes reasonable to estimate $\Gamma_{s\sigma}$ using a somewhat naive spin-wave approximation. As the staggered magnetization in different domains of typical size ξ are oriented in different directions, we have to make a local spin-wave expansion, averaging then $\Gamma_{s\sigma}$ over the directions of the order parameter. Since the one-magnon processes are forbidden for low frequencies, the main contribution to $\Gamma_{s\sigma}$ comes from the correlation function $K_\sigma^{zz}(0)$. Standard calculations in the antiferromagnetic spin-wave (AFSW) approximation give (see Ref. 26 and Appendix B):

$$\Gamma_{s\sigma}({\rm AFSW})=\frac{2\sqrt{2}}{\alpha^3\pi\hbar}\left[\frac{J_{s\sigma}^2}{J_0}\right]\left[\frac{k_BT}{J_0}\right]^2\left[\frac{\xi}{a}\right]$$
$$=\gamma_{\rm AFSW}(\xi)\cdot T^2\ , \tag{21}$$

where $\alpha=\frac{1}{2}\langle\sigma_z\rangle$ is the local order parameter. With the same parameters as above and $\langle\sigma_z\rangle=0.605$,[27] (21) leads

to $\Gamma_{s\sigma}(\text{AFSW}) \sim 1.3\times10^{11}\times(\xi/a)\ \text{sec}^{-1}$.

If one accepts any of these estimations, the ESR linewidth would be incredibly larger than the Larmor ESR frequency for any reasonable value of (ξ/a). It means there is no chance to observe the ESR of impurities if the Cu spins would remain in the equilibrium state. The fact that we are able to observe a Mn-ESR suggests an existence of the bottleneck regime and indirectly proves the inequality (13).

Let us discuss now the relaxation rates Γ_{sL} and $\Gamma_{\sigma L}$ of impurities and Cu ions to the lattice. We can distinguish two main contributions to these rates—the distribution of local fields narrowed by the exchange interactions and relaxation to quasiparticles of the lattice (bath):

$$\Gamma_{iL}=\Gamma_{iL}^{\text{lf}}+\Gamma_{iL}^{\text{qp}}\ ,\quad i=s,\sigma\ . \tag{22}$$

Chakravarty and Orbach[6] consider the Dzyaloshinkii-Moria interactions between Cu ions in undoped La_2CuO_4 as the main source of the broadening of the Cu ESR line. They found that due to the critical fluctuations the narrowing of the ESR line is ineffective, which leads to the enormous value for the $\Gamma_{\sigma L}^{\text{lf}}\sim 34$ kG at room temperature. Later Lazuta[7] argued that the Dzyaloshinkii-Moria interactions do not couple the homogeneous precession of spins and staggered magnetization and gave the estimation for $\Gamma_{\sigma L}^{\text{lf}}$ only 1.5 kG at room temperature. The same order of magnitude gives the magnetic dipole-dipole interactions between Cu ions. We believe that this term $\Gamma_{\sigma}^{\text{lf}}$ can be neglected in comparison with $\Gamma_{\sigma L}^{\text{qp}}$ in Sr-doped cuprates. In the case of localized d electrons it would be just the Korringa relaxation from Cu ions to oxygen holes in the CuO_2 layer. It is known, however, that the structure of quasiparticles of the bath is more complicated having a mixed oxygen and Cu holes nature. We do not attempt here to estimate $\Gamma_{\sigma L}^{\text{qp}}$ explicitly, but if we accept that the total magnetic moment of Cu ions relaxes to quasiparticles having a sharp Fermi surface, $\Gamma_{\sigma L}^{\text{qp}}$ should be proportional to temperature

$$\Gamma_{\sigma L}^{\text{qp}}=B_{\sigma}T \tag{23}$$

because of the factor $f(\epsilon)[1-f(\epsilon)]$, appearing under the integral over energy in the relaxation rate due to scattering of the Fermi quasiparticles [$f(\epsilon)$ is the Fermi function]. The same temperature dependence should be also for Γ_{sL}^{qp}, but in the case of Mn impurity, we expect that Γ_{sL}^{qp} is considerably less in comparison with $\Gamma_{\sigma L}^{\text{qp}}$. The reasons for this are the S state of Mn^{2+}, $d_{x^2-y^2}$ character of the Cu^{2+} ground state, and a strong spin-orbital coupling of Cu ions, as we have already discussed in Sec. III B and having in mind that $\Gamma_{sL}^{\text{qp}}\sim J_{sL}^2$.

The field distribution contribution to the ESR linewidth of Mn is strongly reduced in the bottleneck regime and Γ_{sL}^{lf} is actually presented in this case by the term (15c). The already mentioned contributions to $\langle(\Delta\omega)^2\rangle$—the fine and hyperfine structure, dipole-dipole interactions are not sufficient to explain the observed linewidth at low temperatures. We believe that a possible candidate for the additional increasing of $\langle(\Delta\omega)^2\rangle$ could be anisotropic spin-spin interactions between impurities via antiferromagnetic spin waves (see Appendix A). This interaction can appear only if the distance between impurities is much less in comparison with the size of a "domain" in the paramagnetic phase (the order of magnitude of ξ), and the rotation of the local order parameter is not too fast to smash the anisotropy of the spin-wave-induced spin-spin interactions.

It is worth mentioning also the contribution to the effective ESR linewidth coming from the anisotropic part of the exchange interaction between impurities and Cu ions (3b), since the corresponding contribution to the effective relaxation rate $\delta\Gamma_{s\sigma}(\omega)$,

$$\delta\Gamma_{s\sigma}(\omega)=\left[\frac{\Delta J_{s\sigma}^{z}}{\hbar}\right]^2\frac{1}{2N_{\text{pl}}}\sum_{\mathbf{q}}f(\mathbf{q})K_{\sigma}^{zz}(\mathbf{q},\omega-\omega_s^*) \tag{24}$$

is not bottlenecked and gives rise to the ESR linewidth. We have no information on a possible value of $\Delta J_{s\sigma}^{z}$, but we can expect that this part of the linewidth should not depend on Mn concentration.

IV. INTERPRETATION OF EXPERIMENTAL RESULTS

A. Determination of kinetic parameters from ESR measurements

Before we start to consider the experimental results in terms of our model for spin dynamics in $La_{2-x}Sr_xCuO_{4+\delta}$ doped with Mn we summarize its main features and make a more definite choice of fitting parameters. We assume that in a consequence of the strong exchange coupling between Mn and Cu ions and almost coincidental of their Larmor frequencies, the system displays a collective motion of the total magnetic moments of the Mn and Cu ions. We suppose that the relaxation of Cu and Mn ions to the lattice is ineffective to destroy this collective mode. Since the relaxation rate $\Gamma_{s\sigma}$ between the two spin systems is strongly dependent on temperature and decreases with $T\rightarrow 0$, we have to take into account explicitly the contribution (15c) from the local field distribution and use (1a) for the fitting procedure. Here we limit ourself to the case of a "relaxation-dominated" bottleneck omitting the molecular field λ from (15c) and would like to restate that χ_s^0 and χ_{σ}^0 are the bare susceptibilities without a mutual influence of the Mn and Cu ions against χ_s and χ_{σ}. Since we did not succeed in our attempt to fit the measured value $\chi_s+\chi_{\sigma}$ with a simple molecular field model for the whole temperature region (see below), we use for the fitting procedure of ΔH as the total magnetic susceptibility our measured values.

To reveal the temperature dependence of the linewidth we set in accordance with our model [see Eqs. (19)–(21) and (23)]

$$\Gamma_{s\sigma}=\gamma(\xi)T^{\alpha}\ ,\quad \Gamma_{iL}=B_iT\ ,\quad i=s,\sigma\ . \tag{25}$$

In order to reduce the number of fitting parameters we use explicitly our assumption $\Gamma_{sL}\ll\Gamma_{\sigma L}$, since this term does not change qualitatively the temperature depen-

dence of ΔH. Finally we arrive at a very simple expression which has been used to fit our experimental results of the ESR linewidth,

$$\Delta H = \frac{A}{T^{\alpha}} + \frac{\chi_{\sigma}^{0}}{\chi_s + \chi_{\sigma}} BT + \Delta H_0 \ , \qquad A = \frac{\langle (\Delta\omega)^2 \rangle}{g_s \mu_B \gamma(\xi)} \ . \tag{26}$$

Here we have introduced a usual additional term, "a residual linewidth" ΔH_0, which should not be dependent upon either temperature or Mn concentration. The fitting parameter A and B are determined practically independently by the low- and high-temperature regions. In particular the value of $\gamma(\xi)$, entering in (26) is important only at low temperatures where, as we expect, it should not depend on temperature. The bare spin susceptibility of Cu ions χ_{σ}^{0} has been taken from measurements.[13] Our best fit gives for α in (26) the value slightly varying around $\alpha=2$ with $\gamma(\xi)$ independent of T, so we use further everywhere $\alpha=2$. The results of our fitting are presented in Figs. 7–9 and in Tables I and II.

The Mn concentration dependence is shown in Table I for the sample with the highest Sr doping (Fig. 9). According to our model the dependence of the ESR linewidth on Mn concentration y at high temperatures is entirely controlled by the spin susceptibility of Mn, leaving parameter B in (25) and (26) independent on y. The results of our fitting clearly confirm this statement. The Korringa law for the temperature dependence of the relaxation rate of Cu spins to the bath $\Gamma_{\sigma L}$ (25) is also very well confirmed with some deviations only for the lowest concentration of Mn ($y=0.01$)—see the high-temperature regions in Figs. 7–9. Concerning the Mn concentration dependence of parameter A, we have expected on the contrary to B a linear dependence on y, if the local field distribution $\langle (\Delta\omega)^2 \rangle$ in (26) comes mainly from the anisotropic spin-spin interactions of the Mn ions, presumably due to indirect interactions via antiferromagnetic spin waves as discussed in connection with formula (15c) (see also Appendix A). In this case $\langle (\Delta\omega)^2 \rangle$ and correspondingly A should be proportional to y, and this is the reason why we have set the ratio A/y in Table I. The experimental results clearly show also that A/y is almost independent of y giving strong support to our point of view (we cannot exclude the y dependence of the correlation length ξ). As a matter of fact, the constants A and B are fitted only for one curve and the others were reproduced just by changing y.

Table II shows the Sr concentration dependence of parameters under consideration after averaging A/y and B over y. The constant B certainly increases with the Sr concentration indicating the presence of the channel of relaxation connected with the quasiparticles appearing

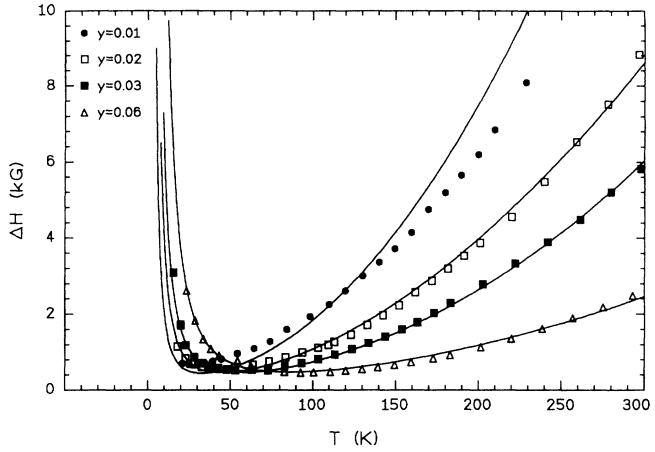

FIG. 8. A model fit (solid line) of the temperature dependence of Mn^{2+} ESR linewidth for $La_{1.8}Sr_{0.2}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.01$, 0.02, 0.03, and 0.06 according to (26). The fit parameters are given in Tables I and II. In (26) we used the measured total susceptibility for this fit.

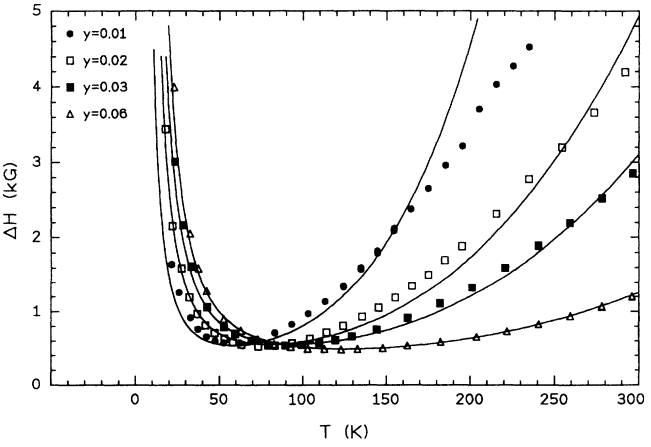

FIG. 7. A model fit (solid line) of the temperature dependence of Mn^{2+} ESR linewidth for $La_{1.9}Sr_{0.1}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.01$, 0.02, 0.03, and 0.06 according to (26). The fit parameters are given in Tables I and II. In (26) we used the measured total susceptibility for this fit.

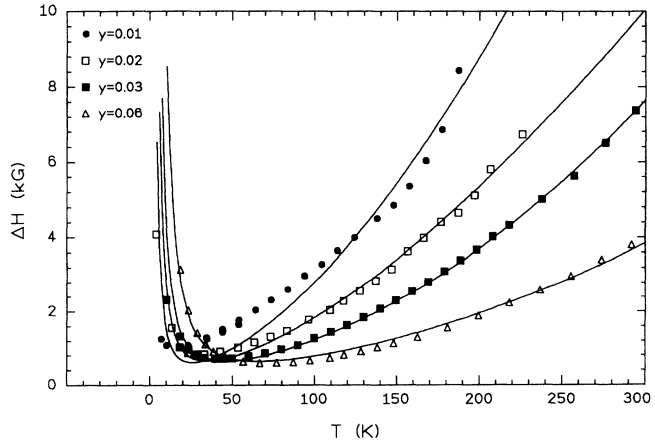

FIG. 9. A model fit (solid line) of the temperature dependence of Mn^{2+} ESR linewidth for $La_{1.7}Sr_{0.3}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.01$, 0.02, 0.03, and 0.06 according to (26). The fit parameters are given in Tables I and II. In (26) we used the measured total susceptibility for this fit.

TABLE I. The Mn concentration dependence of fit parameters of Eq. (26) for the ESR linewidth in $La_{1.7}Sr_{0.3}Cu_{1-y}Mn_yO_{4+\delta}$ with $\alpha=2$ and $\Delta H_0=0.2$ kG.

Mn (y)	A/y (10^{-4} kG K^2)	B [kG/K]
0.01	1.3	0.047
0.02	1.3	0.060
0.03	1.4	0.047
0.06	1.5	0.050

with the Sr doping. According to (10) and (12a) $\Gamma_{\sigma L}$ is proportional to dynamical spin susceptibility of the lattice $\Gamma_{\sigma L}=BT\sim T\,\mathrm{Im}\chi_L(\omega)/\omega$ or, if one can speak in terms of relaxation of the Cu total magnetic moment to the oxygen holes, to $T\,\mathrm{Im}\chi_{\mathrm{holes}}(\omega)/\omega$. The constant $A\sim\langle(\Delta\omega)^2\rangle$ is strongly decreasing with doping, which is not surprising in terms of our model since the coupling between Mn ions via the local antiferromagnetic spin waves should be destroyed with strong enough doping.

B. Reduction of magnetic susceptibility by exchange interactions

The measured static susceptibility of $La_{2-x}Sr_xCuO_{4+\delta}$ doped with Mn should not be just the sum of the Curie susceptibility of Mn and the susceptibility of Cu ions without magnetic impurities $\chi_{\mathrm{total}}\neq\chi_s^0+\chi_\sigma^0$. The simplest molecular-field theory according to (14) gives

$$\chi_{\mathrm{total}}=\chi_s+\chi_\sigma=\frac{\chi_s^0(1+2\lambda\chi_\sigma^0)+\chi_\sigma^0}{1-\theta/T} \tag{27}$$

with $\theta/T=\lambda^2\chi_\sigma^0\chi_s^0$. However, this does not take into account indirect coupling of Mn ions via the oxygen orbitals and only roughly includes a possible interaction via antiferromagnetic spin waves. It seems that one should leave θ as a fitting parameter comparing (27) with experimental measurements. The experimental value of χ_σ^0 for Cu ions without Mn can be taken from the literature.[13] The best fit procedure shows that θ is not large, changing in sign. To reduce the number of fitting parameters we set $\theta=0$. In order to estimate the coupling constant λ in (8a) and (27) we use the temperature region till 150 K, where χ_s certainly dominated. Figure 10 represents results of our fitting for $La_{1.7}Sr_{0.3}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.02$, 0.03, and 0.06, which is, as a matter of fact, not perfect. An estimated value $J_{s\sigma}\sim-300$ K differs not too much from that of $|J_{s\sigma}|=200$ K which we have used in our discussion of $\Gamma_{s\sigma}$. Nevertheless some discrepancy of the temperature dependence at high temperatures is evident and we should mention some reasons for that. First, we did not take into account a contribution from fluctuations of the Cu magnetization in the second order in $J_{s\sigma}$ which could be considerable in the case of two dimensions. Second, an influence of oxygen holes, which can also reduce the Mn susceptibility in the case of antiferromagnetic exchange integral J_{sL}, has been entirely ignored. Moreover, we cannot exclude in this case a coherent localized state of holes on a square of O atoms around Mn ions to form a paramagnetic center with $S=\frac{3}{2}$ in the ground state (similarly to Zhang-Rice singlet[28]) giving the Curie-law temperature dependence with a reduced Curie constant. The number of such localized holes should depend both on the Mn and Sr concentration which was actually observed.

TABLE II. The Sr concentration dependence of averaged fit parameters (see the text) of Eq. (26) for the ESR linewidth in $La_{2-x}Sr_xCu_{1-y}Mn_yO_{4+\delta}$ with $\alpha=2$ and $0.01\le y\le0.06$.

Sr (x)	$(A/y)_{\mathrm{av}}$ (10^{-4} kG K^2)	$(B)_{\mathrm{av}}$ [kG/K]	ΔH_0
0.1	4.2	0.028	0.1
0.2	2.0	0.031	0.3
0.3	1.4	0.051	0.2

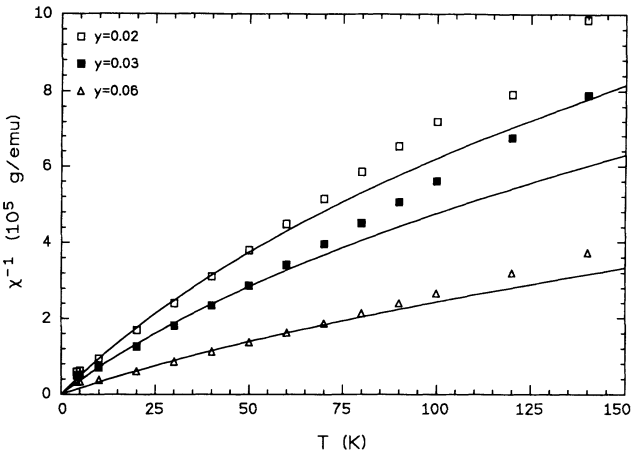

FIG. 10. A fit of the total reciprocal magnetic susceptibility for $La_{1.7}Sr_{0.3}Cu_{1-y}Mn_yO_{4+\delta}$ with $y=0.02$, 0.03, and 0.06 according to (27). The exchange integral $J_{s\sigma}$ was estimated to ~300 K.

V. CONCLUSION

We have investigated the spin dynamics of the system $La_{2-x}Sr_xCuO_{4+\delta}$ doped with Mn using measurements of ESR signal, magnetic susceptibility, and resistivity of the samples in a broad region of temperatures and concentrations of Mn and Sr. We found that the spin system of the Mn impurities and the Cu ions displays a collective motion of their total magnetic moments $\mathbf{M}_s$ and $\mathbf{M}_\sigma$ (bottleneck regime), which is the consequence of a relatively strong isotropic exchange interaction between the Mn and Cu ions, almost coincidental of their Larmor frequencies. The relaxation rate $\Gamma_{s\sigma}$ between Mn and Cu systems is strongly dependent on temperature giving the opportunity to vary the bottleneck regime. At high temperature the coupling $\mathbf{M}_s$ and $\mathbf{M}_\sigma$ is so strong that the relaxation rate $\Gamma_{s\sigma}$ is practically eliminated from the ESR linewidth. It provides an opportunity to investigate the temperature and concentration dependence of the relaxation rate $\Gamma_{\sigma L}$ of Cu to quasiparticles of the lattice in La_2CuO_4 doped by Sr. We have found that in a broad re-

gion of temperatures 50–300 K, $\Gamma_{\sigma L}$ linearly increases with temperature and nonlinearly with concentration of Sr. The $\Gamma_{\sigma L}$ relaxation rate for the Sr-undoped La_2CuO_4 does not depend on temperature for $T \geq 80$ K (Fig. 4). We can conclude that the doping with Sr opens a new channel of relaxation for the Cu spins to bath. The linear temperature dependence of $\Gamma_{\sigma L}$ can be simply explained if the quasiparticles participating in the relaxation of Cu spins to the lattice have a well established Fermi surface for low-frequency excitations.

The broadening of the ESR line at low temperatures can be entirely attributed to the opening of the bottleneck, what reveals according to our model the contribution to the ESR linewidth from the anisotropic spin-spin interactions between Mn ions, reduced by the bottleneck regime. The observed temperature dependence of the corresponding relaxation rate at low temperatures $\Gamma_{s\sigma} \sim T^2$ is consistent with a simplified picture of relaxation due to two-magnon processes existing even in a paramagnetic phase as a consequence of a two-dimensionality of the system. It seems that the ESR measurements of S-state impurities in cuprates give an additional effective tool for investigation of spin dynamics and for comparison of different approaches concerning the nature of spin correlations in the CuO_2 layers of doped cuprates.

ACKNOWLEDGMENTS

We are grateful to R. Orbach for discussions and K. A. Müller for valuable comments on the manuscript. B.I.K. thanks the Technische Hochschule Darmstadt for the hospitality and "Heraeus-Foundation" and DFG-Sonder-forschungsbereich SFB 252 for the support during his visit.

APPENDIX A

An indirect interaction between the two Mn ions at the lattice sites $\mathbf{r}_1=\mathbf{R}$ and $\mathbf{r}_2=\mathbf{0}$ in the CuO_2 plane can appear due to the polarization of the strongly correlated Cu spin system by the Mn-Cu interaction (3a). Here we reproduce for convenience standard calculations in spin-wave approximation. In the case of axial symmetry an effective Hamiltonian of this interaction has the form

$$\mathcal{H}_{\text{eff}}(\mathbf{R})=J_{\perp}(\mathbf{R})(S_1^xS_2^x+S_1^yS_2^y)+J_{\parallel}(\mathbf{R})S_1^zS_2^z \ , \qquad \text{(A1)}$$

where $J_{\perp}(\mathbf{R})$ and $J_{\parallel}(\mathbf{R})$ can be written in terms of the local-spin susceptibility tensor $\chi_{\alpha\beta}(\mathbf{r},\omega)$ of the Cu spin system

$$\begin{aligned} J_{\perp}(\mathbf{R})&=4J_{s\sigma}^2\sum_{\delta\rho}\chi_{\perp}(\mathbf{R}+\delta-\rho,\omega=0) \ , \\ J_{\parallel}(\mathbf{R})&=4J_{s\sigma}^2\sum_{\delta\rho}\chi_{\parallel}(\mathbf{R}+\delta-\rho,\omega=0) \ . \end{aligned} \qquad \text{(A2)}$$

Here the vector δ and ρ connect the sites $\mathbf{r}_1$ and $\mathbf{r}_2$ with their neighbors, and spin susceptibilities are the retarded Green functions. In particular,

$$\begin{aligned} \chi_{\perp}(\mathbf{n}-\mathbf{m},\omega)&=\tfrac{1}{4}\int_{-\infty}^{+\infty}dt\, e^{i\omega t}\langle\langle \sigma_{\mathbf{n}}^x(t)|\sigma_{\mathbf{m}}^x(0)\rangle\rangle \\ &=\tfrac{1}{4}\langle\langle \sigma_{\mathbf{n}}^x|\sigma_{\mathbf{m}}^x\rangle\rangle_{\omega} \ , \qquad \text{(A3)} \\ \langle\langle A(t)|B(0)\rangle\rangle&=-i\Theta(t)\langle\langle A(t)B(0)-B(0)A(t)\rangle\rangle \end{aligned}$$

with $\Theta(t)=1$ for $t>0$ and $\Theta(t)=0$ for $t<0$. An explicit form of $\chi_{\perp}(\mathbf{n}-\mathbf{m},\omega)$ can be found taking into account the local antiferromagnetic ordering of Cu spins in a domain of typical size ξ.

The chain of equations for the transverse Green function in terms of the Cu spin operators $\mathbf{s}_{\mathbf{n}}=\boldsymbol{\sigma}_{\mathbf{n}}/2$

$$\begin{aligned} &\langle\langle \sigma_{\mathbf{n}}^0|\sigma_{\mathbf{m}}^+\rangle\rangle_{\omega}=4\langle\langle s_{\mathbf{n}}^-|s_{\mathbf{m}}^+\rangle\rangle_{\omega} \ , \\ &\omega\langle\langle s_{\mathbf{n}}^-|s_{\mathbf{m}}^+\rangle\rangle_{\omega}=-2\langle s_{\mathbf{n}}^z\rangle\delta_{\mathbf{nm}} \\ &\qquad +J_0\sum_{\delta}\{\langle\langle s_{\mathbf{n}}^-s_{\mathbf{n}+\delta}^z|s_{\mathbf{m}}^+\rangle\rangle_{\omega} \\ &\qquad\qquad -\langle\langle s_{\mathbf{n}}^zs_{\mathbf{n}+\delta}^-|s_{\mathbf{m}}^+\rangle\rangle_{\omega}\} \end{aligned} \qquad \text{(A4)}$$

can be truncated by a usual decoupling:

$$\begin{aligned} \langle\langle s_{\mathbf{n}}^zs_{n+\delta}^-|s_{\mathbf{m}}^+\rangle\rangle_{\omega}&=\nu\langle\langle s_{\mathbf{n}+\delta}^-|s_{\mathbf{m}}^+\rangle\rangle_{\omega} \ , \\ \langle\langle s_{\mathbf{n}}^-s_{\mathbf{n}+\delta}^z|s_{\mathbf{m}}^+\rangle\rangle_{\omega}&=-\nu\langle\langle s_{\mathbf{n}}^-|s_{\mathbf{m}}^+\rangle\rangle_{\omega} \ . \end{aligned} \qquad \text{(A5)}$$

Here the order parameter $\nu=\langle s_{\mathbf{n}}^z\rangle=-\langle s_{\mathbf{n}+\delta}^z\rangle$ for two magnetic sublattices is introduced.

Performing the Fourier transform $\mathbf{n}\rightarrow\mathbf{q}$ separately for the Green functions of spins, belonging to the same sublattice and for different ones,

$$\begin{aligned} G_1(\mathbf{q},\omega)&=\sum_{\mathbf{m}}{}'\langle\langle s_{\mathbf{n}}^-|s_{\mathbf{m}}^+\rangle\rangle e^{i\mathbf{q}(\mathbf{n}-\mathbf{m})} \ , \\ G_2(\mathbf{q},\omega)&=\sum_{\mathbf{m}}{}'\langle\langle s_{\mathbf{n}+\delta}^0|s_{\mathbf{m}}^+\rangle\rangle e^{i\mathbf{q}(\mathbf{n}+\delta-\mathbf{m})} \ , \end{aligned} \qquad \text{(A6)}$$

we arrive at the set of equations

$$\begin{aligned} &(\omega+\nu z_0)G_1(\mathbf{q},\omega)+\nu z\gamma_{\mathbf{q}}J_0G_2(\mathbf{q},\omega)=-2\nu \ , \\ &-\nu z\gamma_{\mathbf{q}}J_0G_1(\mathbf{q},\omega)+(\omega-\nu zJ_0)G_2(\mathbf{q},\omega)=0 \ , \end{aligned} \qquad \text{(A7)}$$

where z is the number of the nearest ions,

$$\gamma_{\mathbf{q}}=\frac{1}{z}\sum_{\delta}e^{i\mathbf{q}\delta} \qquad \text{(A8)}$$

and the sum in (A6) is running over the sublattice sites only.

The solution of (A7) is evident:

$$\begin{aligned} G_1(\mathbf{q},\omega)&=\frac{\nu}{\varepsilon_{\mathbf{q}}}\left\{\frac{\nu zJ_0-\varepsilon_{\mathbf{q}}}{\omega-\varepsilon_{\mathbf{q}}}-\frac{\nu zJ_0+\varepsilon_{\mathbf{q}}}{\omega+\varepsilon_{\mathbf{q}}}\right\} \ , \\ G_2(\mathbf{q},\omega)&=-\frac{\nu z\gamma_{\mathbf{q}}J_0}{\varepsilon_{\mathbf{q}}}\left\{\frac{1}{\omega-\varepsilon_{\mathbf{q}}}-\frac{1}{\omega+\varepsilon_{\mathbf{q}}}\right\} \ . \end{aligned} \qquad \text{(A9)}$$

The magnon energy $\varepsilon_{\mathbf{q}}$ is linear in the long-wave limit:

$$\varepsilon_{\mathbf{q}}=\nu zJ_0\sqrt{1-\gamma_{\mathbf{q}}^2}\approx\frac{1}{\sqrt{2}}\nu zJ_0aq \qquad \text{(A10)}$$

and the Green functions $G_1(\mathbf{q},0)$ and $G_2(\mathbf{q},0)$ are divergent as $1/q^2$. At the same time we expect that spin waves exist only at $q>1/\xi$ in the system having no long-range

order, and we remove the divergence by replacing $q^2 \to q^2 + 1/\xi^2$,

$$G_1(\mathbf{q},0) = -G_2(\mathbf{q},0) = \frac{4}{za^2 J_0 (q^2 + 1/\xi^2)} . \quad \text{(A11)}$$

Collecting (A2), (A3), (A6), and (A11) and performing the Fourier transform of (A12) we have for $R \gg a$

$$J_\perp(\mathbf{R}) = \frac{2}{\pi}\left[\frac{J_{s\sigma}^2}{J_0}\right]\sum_{\delta\rho} K_0\left[\frac{|\mathbf{R}+\delta-\rho|}{\xi}\right]\cos(\mathbf{RQ})$$
$$\approx z^2\left[\frac{J_{s\sigma}^2}{J_0}\right]\sqrt{(2\xi/\pi R)}\,e^{-R/\xi}\cos(\mathbf{RQ}) \quad \text{(A12)}$$

where $\cos(\mathbf{RQ})$ with $\mathbf{Q}=(\pi/a,\pi/a)$ reflects the opposite sign of G_1 and G_2 in (A11) and $K_0(x)$ is the function of MacDonald.

The same approximation gives for the longitudinal part of the interaction $J_\parallel(R) \ll J_\perp(R)$, what results in a highly anisotropic $\mathcal{H}(\mathbf{R})$ in (A1). The contribution of this interaction to $\langle(\Delta\omega)^2\rangle$ is

$$\langle(\Delta\omega)^2\rangle = \frac{S(S+1)}{3\hbar^2}\sum_{\mathbf{R}}[J_\perp(\mathbf{R}) - J_\parallel(\mathbf{R})]^2 \cdot y$$
$$\approx \frac{2S(S+1)}{3}\left[\frac{z^2 J_{s\sigma}^2}{\hbar J_0}\right]^2\left[\frac{\xi}{a}\right]^2 \cdot y , \quad \text{(A13)}$$

where y and S are the concentration and the spin of Mn ions. The value of $\langle(\Delta\omega)^2\rangle$ in (A13) is certainly overestimated since we did not actually make the averaging over the orientations of order parameter relative to the external magnetic field and our approximations (A6) and (A11) are simplified, exaggerating the difference between $J_\perp$ and $J_\parallel$ (see, however, remarks on a susceptibility anisotropy[29]).

APPENDIX B

For the estimation of the longitudinal contribution to $\Gamma_{s\sigma}$ we can use the result (A10). It is convenient to rewrite this part of $\Gamma_{s\sigma}$:

$$\Gamma_{s\sigma}(\omega_s^*) = \frac{1}{2}\left[\frac{J_{s\sigma}}{\hbar}\right]^2\sum_{\delta\rho}\int_{-\infty}^{+\infty} dt\,\langle\sigma_\delta^z(0)\sigma_\rho^z(t)\rangle . \quad \text{(B1)}$$

Using the relation $\sigma^z = 2s^- s^+ - 1$, we can decouple the correlation function of (B1), taking into account only its fluctuating part

$$\langle\sigma_\delta^z(0)\sigma_\rho^z(t)\rangle \simeq 4\langle s_\delta^+(0)s_\rho^-(t)\rangle\langle s_\delta^-(0)s_\rho^+(t)\rangle . \quad \text{(B2)}$$

Similar to (6b) we have

$$\langle s_\delta^+(0)s_\rho^-(t)\rangle = \frac{1}{N_{\rm pl}}\sum_{\mathbf{q}}\int\frac{d\omega}{2\pi}K_1^{+-}(\mathbf{q},\omega)e^{i\mathbf{q}(\rho-\delta)-i\omega t} , \quad \text{(B3)}$$

where $\mathbf{q}$ is running as against (6a) over a half of the BZ. The spectral density $K_1^{+-}(\mathbf{q},\omega)$ is directly connected with the Green function $G_1(\mathbf{q},\omega)$ (A9):

$$K_1^{+-}(\mathbf{q},\omega) = -2n(\omega)\,\mathrm{Im}G_1(\mathbf{q},\omega+i\varepsilon) ,$$
$$K_1^{-+}(\mathbf{q},\omega) = e^{-\hbar\omega/k_BT}K_1^{+-}(\mathbf{q},-\omega) , \quad \text{(B4)}$$
$$n(\omega) = \frac{1}{e^{\hbar\omega/k_BT}-1} , \quad \varepsilon \to +0 .$$

Substituting (B2), (B3), (B4), and (A9) into (B1) we have

$$\Gamma_{s\sigma}(\omega_s^*) = 8\pi z^2\left[\frac{J_{s\sigma}}{\hbar}\right]^2\left[\frac{2}{N_{\rm pl}}\right]^2$$
$$\times\sum_{\mathbf{q}\mathbf{q}'}\frac{(\nu z J_0)^2 - \varepsilon_{\mathbf{q}}\varepsilon_{\mathbf{q}'}}{\varepsilon_{\mathbf{q}}\varepsilon_{\mathbf{q}'}}n(\varepsilon_{\mathbf{q}'})$$
$$\times[1+n(\varepsilon_{\mathbf{q}'})]\delta(\varepsilon_{\mathbf{q}}-\varepsilon_{\mathbf{q}'}) . \quad \text{(B5)}$$

Since the main contribution in the sums (B5) comes from $\varepsilon_{\mathbf{q}} < k_BT$, we can use the long-wave approximation (A10). Converting the sums over $\mathbf{q}$ into integrals,

$$\frac{2}{N_{\rm pl}}\sum_{\mathbf{q}} \to \int_\Delta^\infty d\varepsilon\,\rho(\varepsilon) , \quad \rho(\varepsilon) = \frac{2\varepsilon}{\pi(\nu z J_0)^2} ,$$
$$\Delta = \frac{\nu z J_0}{\sqrt{2}}\left[\frac{a}{\xi}\right] , \quad \text{(B6)}$$

we have

$$\Gamma_{s\sigma}(\omega_s^*) = \frac{8}{\nu^2\pi\hbar}\left[\frac{J_{s\sigma}^2}{J_0}\right]^2\left[\frac{k_BT}{J_0}\right]\frac{1}{e^{\Delta/k_BT}-1} , \quad \text{(B7)}$$

which is reduced to (21) in the text if $\Delta \ll k_BT$.

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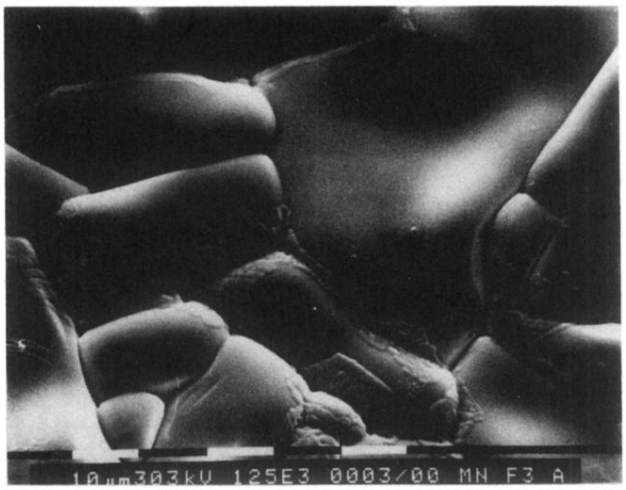

FIG. 1. Microprobe photograph for polycrystalline $La_{1.8}Sr_{0.2}Cu_{0.98}Mn_{0.02}O_{4+\delta}$.