Intrinsic EPR in $La_{2-x}Sr_xCuO_4$: Manifestation of Three-Spin Polarons

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Electron-paramagnetic resonance (EPR) measurements on $La_{2-x}Sr_xCuO_4$ provide experimental evidence of a three-spin polaron, consisting of two Cu^{2+} ions and one p hole. The symmetry properties and the peculiar temperature dependence of the g values of the EPR line indicate the presence of dynamical Jahn-Teller distortions and formation of a collective mode of polarons and surrounding strongly correlated Cu ions (bottlenecked regime). [S0031-9007(97)04581-X]

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The nature and electronic structure of the quasiparticles which originate from the doped p holes in the CuO_2 planes of the high-temperature superconductors still remain a controversially discussed subject. Also the initial belief that the study of spin and charge dynamics of the low-doped parent compounds can reveal the basic elements and mechanisms of the insulator to metal transition still has to be realized. Attempts to investigate the spin dynamics of the bulk Cu-spin system by Cu^{2+} electron-paramagnetic resonance (EPR) measurements failed: the EPR signal in the parent compound La_2CuO_4 could not be observed at all, and the EPR absorption observed in the doped samples in most cases was related to surface defects, to paramagnetic defect centers in the bulk material, or to small amounts of the green phase [1,2]. Nevertheless, measurements using Mn^{2+} ions as EPR probe in $La_{2-x}Sr_xCuO_4$ ceramics [3] have revealed a strong isotropic exchange coupling between Mn^{2+} and Cu^{2+} ions, giving rise to a collective mode and providing the opportunity to estimate the relaxation rate $\Gamma_{\sigma L}$ of the Cu-spin system to the lattice. It has been found that at high temperatures $\Gamma_{\sigma L}$ can be approximated by a linear function $\Gamma_{\sigma L} = B_\sigma T$ with a slope $B_\sigma \simeq 35$–40 G/K. Based on these experiments a very broad intrinsic Cu^{2+} line can be expected at elevated temperatures which, however, should be observable in an optimized experiment. In this Letter we report a study of the spin dynamics in $La_{2-x}Sr_xCuO_4$ by EPR using no additional spin probes. The results are interpreted in terms of a "three-spin polaron" (TSP) existing in the hole-doped CuO_2 planes. The TSP consists of two Cu^{2+} ions and one p hole and is distorted due to a dynamical Jahn-Teller (JT) effect.

The EPR experiments were performed at X-band frequencies (9.1 GHz) on single-crystalline samples of $La_{2-x}Sr_xCuO_4$. All crystals were prepared using spontaneous crystallization from a CuO flux [4,5]. For the crystals with Sr-doping levels $0 \leq x \leq 0.2$, for temperatures $20 \leq T \leq 300$ K a broad but well defined single EPR line has been detected [6]. A typical EPR spectrum at 70 K observed in a crystal with $x = 0.075$ is shown in the inset of Fig. 1. Here the field derivative of the absorbed microwave power dP/dH is shown vs the magnetic field H. The line shape indicates a typical metallic behavior. Because of the broad lines, for the line shape analysis it was neccessary to take into account also the negative resonance field which belongs to the counterclockwise polarized microwave field.

The angular dependence of the resonance field for $c \parallel H(\Theta = 0°)$ to $c \perp H(\Theta = 90°)$ [Fig. 1(a)] can be

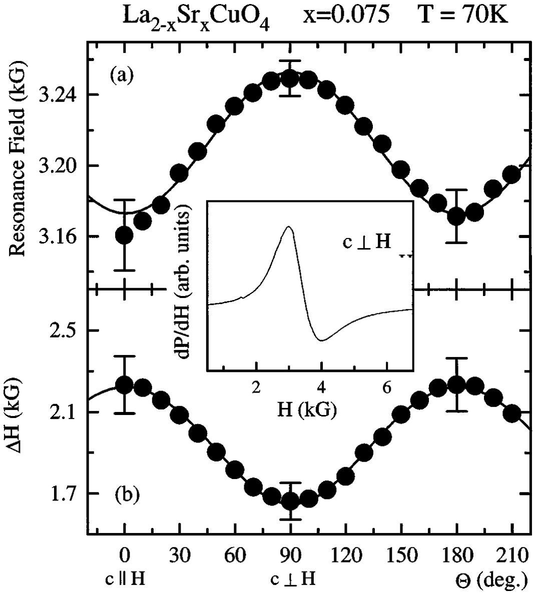

FIG. 1. (a) Angular dependence of the resonance field and (b) of the linewidth ΔH by rotating the c axis with respect to the magnetic field. An axial symmetric behavior is indicated by the solid lines. The inset shows the EPR spectrum with a Lorentzian line shape for the crystal orientation $c \perp H$.

well described with anisotropic g factors with uniaxial symmetry [solid line in Fig. 1(a)]. When the a, b plane is rotated at $\Theta = 90°$ around the c axis, the resonance field and the linewidth are constant for all angles within the accuracy of the measurements. This behavior of the resonance absorption is typical for a paramagnetic center with spin $S = 1/2$. For a center with $S > 1/2$ and an unresolved fine structure one expects a minimum in the angular dependence of the linewidth near $\Theta \approx 60°$ which clearly is not observed and strictly can be excluded [Fig. 1(b)].

The nature of the relaxation mechanism of the EPR probe is reflected by the width ΔH of the EPR absorption. Its temperature dependence for different Sr concentrations is shown in Fig. 2. Distinct minima of the linewidth are observed for all Sr concentrations at temperatures $T_{\min}$. For low doping levels ($x < 0.05$) $T_{\min}$ depends almost linearly on the Sr concentration x as demonstrated in the inset of Fig. 2. This dependency as well as all other EPR parameters is consistent with the EPR results on ceramic samples [7]. The steep increase of the linewidth below $T_{\min}$ seems to be a common feature of all doped and undoped high-T_c superconductors which were investigated by EPR measurements so far [3,7–9]. This increase signals the freezing of spin fluctuations and the concomitant localization of the charge carriers.

The EPR intensity which reflects the static susceptibility of the EPR centers shows a Curie-like behavior at low temperatures, while above $T = 50$ K it is almost constant and characteristic of a Pauli-like spin susceptibility [6]. A similar behavior was also found for the EPR intensity of single crystalline $\mathrm{YBa_2Cu_3O_{6+\delta}}$ [8]. It is important to note that the observed signals in $\mathrm{La_{2-x}Sr_xCuO_4}$ could be related neither to paramagnetic surface defects nor to $\mathrm{Cu^{2+}}$ centers in a disturbed octahedra environment containing oxygen vacancies. Both possibilities yield temperature independent and much narrower spectra [2,4].

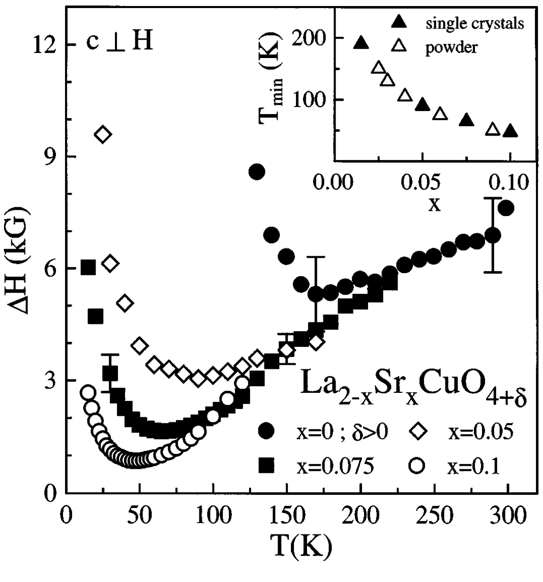

FIG. 2. Temperature dependence of the linewidth ΔH in $\mathrm{La_{2-x}Sr_xCuO_{4+\delta}}$. The inset shows the temperatures $T_{\min}$ of the linewidth minima vs x. The results of measurements with ceramic samples are also included for comparison [7].

As can be seen from Fig. 2, a signal was also observed in nominally pure $\mathrm{La_2CuO_{4+\delta}}$. The antiferromagnetic phase transition in this material was found to be close to 150 K, indicating substantial excess of oxygen δ. To reduce δ the undoped ($x = 0$) material has been annealed in argon atmosphere at 1200 K. Then the EPR signal vanishes completely in accord with previous findings [1,2]. It is worth mentioning that in [1] no EPR signal was found in the pure $\mathrm{La_2CuO_4}$ in the temperature range up to 1150 K. Therefore we attribute the EPR absorption to magnetic centers created by p holes doped either by excess oxygen or by Sr ions. What can be said about the nature of the paramagnetic (pm) center observed by EPR? The p hole itself is out of consideration, and can be excluded since a very strong p-d coupling yields a Zhang-Rice singlet with $S = 0$. Good candidates for the pm center under consideration could be large ferromagnetic or pseudo-Jahn-Teller polarons which have recently been suggested by Hizhnyakov and Sigmund [10], and by Bersuker and Goodenough [11]. However, the very specific behavior of the experimental g factors, intensities, and linewidths impose strong experimental constraints for the choice of a model for this pm center. In particular, the complete absence of an even unresolved fine structure suggests the total spin of the center to be $S = 1/2$, ruling out the importance of large polarons mentioned above with $S > 1/2$. Considering the absolute value of the EPR intensity for the sample with $x = 0.075$, we have estimated that 1% of the doped holes are included in the formation of pm centers. We expect that isolated pm centers exist in the regions of our samples with a poor concentration of Sr. The simplest and natural choice for the model of the pm center is a three-spin polaron built up by one O-hole spin and two adjacent Cu spins (see Fig. 3). This type of a quasiparticle has been proposed earlier by Emery and Reiter [12] and was considered in detail by Frenkel *et al.* [13] by numerical calculations of the ground-state wave function for a cluster consisting of 16 Cu atoms. The most important experimental evidence for this model can be found by an inspection of the temperature dependence of the g factors (Fig. 4). $g_{\|}$ decreases with decreasing temperature to a rather unusual value $g_{\|} < 2$, showing a crossover with $g_{\perp}$. In principle this value could be attributed to the usual line shift due to an antiferromagnetic superexchange coupling of the polaron to the surrounding Cu ions. For the square lattice this interaction can be written in the following form for the TSP directed along the x axis:

$$H_{\mathrm{int}} = -\frac{1}{\sqrt{N}} \sum_{\mathbf{q}} F_{\mathbf{q}} [J_{\|}^{p} S^{z} \sigma_{\mathbf{q}}^{z} + J_{\perp}^{p} (S^{x} \sigma_{\mathbf{q}}^{x} + S^{y} \sigma_{\mathbf{q}}^{y})], \tag{1}$$

$$F_{\mathbf{q}} = 2 \cos\left(\frac{3}{2} q_x a\right) + 4 \cos(q_y a) \cos\left(\frac{1}{2} q_x a\right),$$

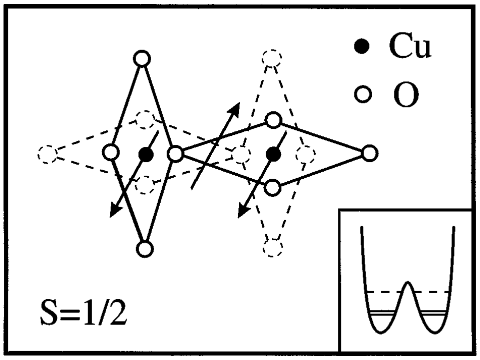

FIG. 3. Three-spin magnetic polaron which is regarded as the EPR active center in the CuO_2 plane. The Jahn-Teller distorted polaron has two degenerated configurations as indicated by the dashed lines. The inset shows the corresponding double-well potential with the excited vibronic state (dashed line) and the ground state split by tunneling (solid lines).

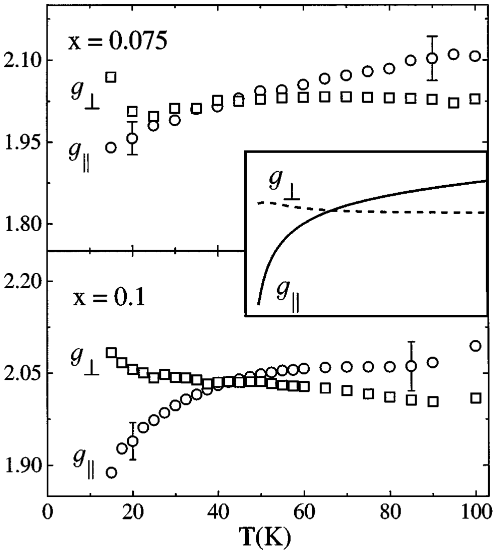

FIG. 4. Temperature dependence of the g factors of $La_{2-x}Sr_xCuO_4$ as determined from the resonance field for two different crystal orientations $c \parallel H$ and $c \perp H$, respectively. The inset demonstrates that the model describes the unusual crossover of the g factors satisfactorily.

where S^α and $\sigma_{\mathbf{q}}^\alpha/2$ are the α components of the spin operators of TSP and Cu ions, respectively. Coordinate and 2D $\mathbf{q}$ representations are used. $J_\parallel^p$ and $J_\perp^p$ are the effective coupling constants between the TSP and the Cu ions; $F_{\mathbf{q}}$ is a form factor including the six neighboring Cu ions. If the external magnetic field is directed along the z axis ($z \parallel c$), in the isothermal regime the line shift $\triangle g_\parallel = \lambda_\parallel \chi_\parallel^\sigma$ is expected, where $\chi_\parallel^\sigma$ is the static susceptibility of the Cu-spin system and $\lambda_\parallel = 2F_{\mathbf{0}} J_\parallel^p / g_\parallel^p g_\parallel^\sigma \mu_B^2$, with $g_\parallel^p$ and $g_\parallel^\sigma$ describing the corresponding g factors of TSP and Cu ions. In the case of antiferromagnetic coupling $\lambda_\parallel < 0$, the value $g_\parallel < 2$ would be obtained with the usual value of Cu-spin susceptibility and the usual Cu-Cu exchange coupling $J_\parallel^p \approx 10^3$ K. However, such an explanation meets, at least, two severe contradictions. First, in the case of H directed perpendicular to the c axis $g_\perp$ should reveal a similar temperature dependence and a similar value of the line shift, since one expects $|J_\parallel^p - J_\perp^p| \ll J_\perp^p$. Figure 4 shows that it is not the case. Second, in the isothermal regime, besides the line shift, the exchange coupling (1) creates a contribution to the linewidth due to the relaxation to the Cu-spin system $\Gamma_{p\sigma}$ similar to the nuclear relaxation rate. Because of the form factor $F_{\mathbf{q}}$, the TSP should not be influenced by the critical spin fluctuations near $\mathbf{q} = (\frac{\pi}{a}, \frac{\pi}{a})$, similar to ^{139}La. The contribution to $\Gamma_{p\sigma}$ can then be easily estimated: $\Gamma_{p\sigma} \approx (J_\parallel^p/A)^2(1/T_1)$, where A is the hyperfine coupling constant and $1/T_1$ is the nuclear relaxation rate. Taking typical values for A and $1/T_1$ we obtain an enormous value $\Gamma_{p\sigma} \approx 10^4$ GHz, which makes the EPR signal not observable at all, even in the case of a considerable reduction of $J_\parallel^p$ due to formation of a polaronic state. Both contradictions can be resolved, if to notice that the relaxation of polarons to the Cu-spin system is much larger than the relaxation rate of the latter to the lattice: $\Gamma_{p\sigma} \gg \Gamma_{\sigma L}$. In this situation the magnetization of the Cu ions cannot remain in an equilibrium state and a collective mode of the polarons and Cu ions is formed making the coupling between them not directly observable (bottleneck effect). Similar observations have been made in the Mn EPR experiments in $La_{2-x}Sr_xCuO_4$:Mn [3]. There is, however, an important distinction in the case of the TSP: a small anisotropy of the interaction (1) has very important consequences because of the large absolute value of the coupling constant. If the interaction (1) would be isotropic, then both the contribution $\Gamma_{p\sigma}$ to the linewidth and the line shift would disappear in the strong bottleneck limit as a consequence of a commutation of the total spin of the two spin subsystems with the isotropic exchange interaction between them [14]. An anisotropic part of the interaction contributes both to the linewidth and to the effective g factor even in the very deep bottleneck regime. To demonstrate this effect we have rederived the coupled equations for the transverse magnetizations of the polarons and Cu-spin system, and we have obtained the following expressions for the effective g factors for the case, when the alternating magnetic field is perpendicular to the c axis:

$$g_\parallel = \frac{\chi_\perp^p g_\parallel^p (1 + \delta\lambda_\parallel \chi_\parallel^\sigma) + \chi_\perp^\sigma g_\parallel^\sigma (1 + \delta\lambda_\parallel \chi_\parallel^p)}{\chi_\perp^p + \chi_\perp^\sigma},$$

$$g_\perp = \frac{\chi_\perp^p g_\perp^p (1 - \frac{1}{2}\delta\lambda_\perp \chi_\perp^\sigma) + \chi_\perp^\sigma g_\perp^\sigma (1 - \frac{1}{2}\delta\lambda_\perp \chi_\perp^p)}{\chi_\perp^p + \chi_\perp^\sigma}, \tag{2}$$

with $\delta\lambda_\parallel = 2F_{\mathbf{0}}(J_\parallel^p - J_\perp^p) g_\parallel^p g_\parallel^\sigma \mu_B^2$ and $\delta\lambda_\perp = \delta\lambda_\parallel (g_\parallel^p g_\parallel^\sigma / g_\perp^p g_\perp^\sigma)$. Equation (2) demonstrates that in addition to the usual terms for the bottlenecked regime there are contributions due to the anisotropy of the coupling constants and g factors. Moreover, comparing

Eq. (2) for $g_{\|}$ and $g_{\perp}$, one can see that the terms with $\delta\lambda_{\|}$ and $\delta\lambda_{\perp}$ enter with an opposite sign. Details of the calculations will be published in a forthcoming paper. It is rather evident that Eq. (2) is consistent with the observed temperature dependence of g factors, if for the polaron spin susceptibility a Curie law $\chi^{p}_{\|,\perp} = C_{\|,\perp}/T$ and for the Cu-spin susceptibility $\chi^{\sigma}_{\|,\perp}$ the values determined by the NMR Knight shift [15] are assumed. Furthermore, we used $g^{\sigma}_{\|} > g^{\sigma}_{\perp}$ as a consequence of the $d_{x^2-y^2}$ state of the Cu^{2+} ion. The quality of the fits is significantly increased, allowing for $g^{p}_{\|,\perp} \neq g^{\sigma}_{\|,\perp}$ and, in addition, $g^{p}_{\|} < g^{p}_{\perp}$. Of course, the g factors of the polaron state should be slightly different from that of the Cu ion because of the mixing with the p hole, but it is not enough to produce the latter inequality. From this observation we can draw a further important conclusion. Obviously the polaron is distorted due to a pseudo-JT effect, in a similar way as described in [11]. However, the competition between the JT distortions with a localization of the Zhang-Rice singlet on one Cu-site and the hopping between two symmetry equivalent JT distortions has to be taken into account. As a result of the JT effect the ground state of the polaron is the mixture of the functions belonging to the Γ_3 representation: $\psi = \cos(\alpha/2)d_{x^2-y^2} + \sin(\alpha/2)d_{3z^2-r^2}$ [16]. The g factors of the polaron for this state are

$$
\begin{aligned}
g^{p}_{1} &= 2 + 2u(2 - \cos\alpha - \sqrt{3}\sin\alpha)\,, \\
g^{p}_{2} &= 2 + 2u(2 - \cos\alpha + \sqrt{3}\sin\alpha)\,, \qquad (3) \\
g^{p}_{3} &= 2 + 4u(1 + \cos\alpha)\,,
\end{aligned}
$$

where u is the strength of the spin-orbital mixing. Because of the tunneling between two equivalent configurations of the polaron (see Fig. 3) the first two g factors are interchanging, giving an averaged value $g^{p}_{\perp} = (g^{p}_{1} + g^{p}_{2})/2$, while the third one remains the same $g^{p}_{\|} = g^{p}_{3}$. As a result the uniaxial symmetry is restored. The temperature dependence of g factors given by Eq. (2) for $\alpha \sim \pi$ is shown in the inset of Fig. 4. Details of the fitting of the temperature dependence of g factors and linewidth will be given elsewhere.

The TSP can move by subsequent tunneling processes. This motion is similar to that described in [11]; however, in our case we have rather a "walking" polaron instead of a "crawling" one. It is worth mentioning that this motion will give an additional contribution to the linewidth due to the spin-orbit coupling, as well as the tunneling between the equivalent configurations inside the polaron. The concentration of the polarons depends, of course, on the Sr doping level. At high enough local concentrations the polarons can coagulate into drops or stripes, which will be EPR silent. This picture is consistent with a very low intensity of the EPR signal for the relatively large concentrations $x = 0.16$ and 0.2. We believe that the detected three-spin polaron could be the basic element of the insulator-metal transition.

In summary, using EPR measurements we provided experimental evidence for the existence of a three-spin polaron in $La_{2-x}Sr_xCuO_4$. The TSP is stabilized by dynamical Jahn-Teller distortions. Despite the strong coupling of these polarons to the Cu-spin system, they remain observable due to the formation of a collective mode with the Cu ions. The anisotropic part of this coupling gives a contribution to the g factors and the linewidth even in the deep bottleneck regime yielding very unusual temperature and angular dependences.

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