Metallic Phase in Lightly Doped $La_{2-x}Sr_xCuO_4$ Observed by Electron Paramagnetic Resonance

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In the low doping range of x from 0.01 to 0.06 in $La_{2-x}Sr_xCuO_4$, a narrow electron paramagnetic resonance (EPR) line has been investigated. This line is distinct from the known broad line and both lines are due to probing Mn^{2+} ions. The narrow line is ascribed to metallic regions in the material, and its intensity increases exponentially upon cooling below ~150 K. The activation energy deduced $\Delta = 460(50)$ K is nearly the same as that found in the doped superconducting regime by Raman and neutron scattering. The intensity of the narrow EPR line follows the same temperature dependence as the in-plane resistivity anisotropy in lightly doped $La_{2-x}Sr_xCuO_4$ single crystals.

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The generic phase diagram in hole-doped cuprates is by now well established. At a critical concentration of doping $x_{c1} \approx 0.06$, superconductivity sets in at $T = 0$, and ends at a higher doping level $x_{c2} \approx 0.25$ [1]. Both are the critical end points of the superconducting phase-transition line [2]. At the former, a transition from an insulating to the superconducting state has been assumed until very recently [2]. However, using finite-size scaling for the susceptibility of a series of concentrations $x < x_{c1}$, the following was inferred: The material consists of antiferromagnetic (AF) domains of variable size, separated by metallic domain walls [3]. More recently Ando *et al.* corroborated this early finding by measuring the in-plane resistivity anisotropy in untwinned single crystals of $La_{2-x}Sr_xCuO_4$ (LSCO) and $YBa_2Cu_3O_{7-\delta}$ in the lightly doped region, interpreting their results in terms of metallic stripes present [4]. Previous electron paramagnetic resonance (EPR) measurements in LSCO at $x = 0.03 < x_{c1}$ revealed, in addition to a broad EPR line observed in the entire doping range x [5], a narrow line [6]. It was interpreted as stemming from the metallic, hole-rich parts in the sample and is distinct from the broad line from the nonconducting hole-poor regions. The latter line showed a clear isotope effect in its linewidth [5,6]; the narrow one did not. In the present letter, we describe a thorough EPR investigation of the behavior of the narrow line for concentrations $0.01 \leq x \leq 0.06$, i.e., below x_{c1}. Of special interest is the exponential increase of the narrow line intensity upon cooling. The activation energy inferred is nearly the same as that deduced from other experiments for the formation of bipolarons [7], pointing to the origin of the metallic stripes present.

The $La_{2-x}Sr_xCu_{0.98}Mn_{0.02}O_4$ polycrystalline samples with $0 \leq x \leq 0.06$ were prepared by the standard solid-state reaction method. The EPR measurements were performed at 9.4 GHz using a BRUKER ER-200D spectrometer equipped with an Oxford Instruments helium flow cryostat. In order to avoid a signal distortion due to skin effects, the samples were ground and the powder was suspended in paraffin. We observed an EPR signal in all samples. The signal is centered near $g \sim 2$, a value very close to the g factor for the Mn^{2+} ion. Figure 1 shows

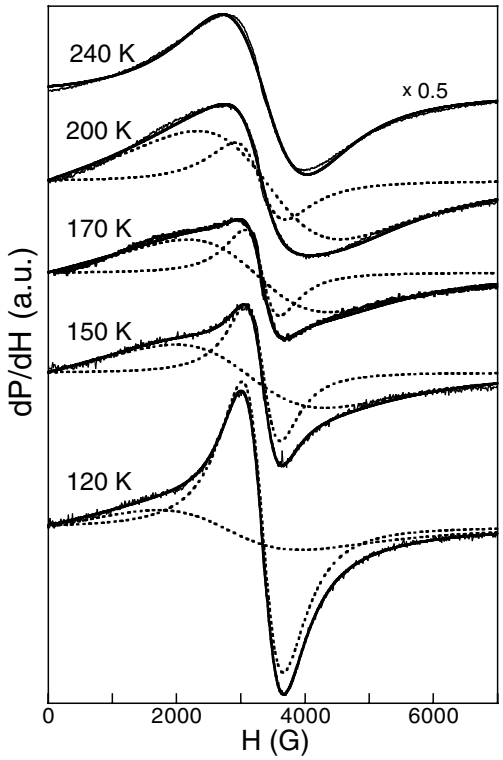

FIG. 1. EPR signal of $La_{1.97}Sr_{0.03}Cu_{0.98}Mn_{0.02}O_4$ at different temperatures. At 240 K, the solid line represents the fit using a single Lorentzian line. At other temperatures the solid lines represent a fit with a sum of two Lorentzians shown by the dotted lines.

typical EPR spectra for the $x = 0.03$ sample at different temperatures. One can see that at 240 K a single EPR line of Lorentzian shape is observed. However, with decreasing temperature a second line appears and the EPR spectra can be well fitted by a sum of two Lorentzians with different linewidths: a narrow one and a broad one. Figure 2 presents the temperature dependence of the linewidths of the two signals. Similar two-component EPR spectra were observed in other samples with different Sr concentrations up to $x = 0.06$. At $x = 0.06$, only a single EPR line is seen in the entire temperature range, in agreement with our previous studies of samples with $0.06 \leq x \leq 0.20$ [5].

Figure 3 shows the temperature dependence of the broad and the narrow EPR signal intensities. One can see that these two signals follow a completely different temperature dependence. The intensity of the broad component has a broad maximum and strongly decreases with decreasing temperature. On the other hand, the intensity of the narrow component is negligible at high temperatures and starts to increase almost exponentially below ~150 K. We note that the temperature below which the intensity of the broad line decreases shifts to lower temperatures with increasing doping. However, the shape of the $I(T)$ dependence for the narrow line is practically doping independent and shifts only slightly towards higher temperatures with increased doping. A similar tendency is observed also for the temperature dependence of the EPR linewidth. The linewidth of the broad component and its temperature dependence are strongly doping dependent, whereas the linewidth of the narrow component is very similar for samples with different Sr doping (see Fig. 2).

It is important to point out that the observed two-component EPR spectra are intrinsic and are not due to conventional chemical phase separation. We examined our samples using x-ray diffraction, and detected no impurity phases. Moreover, the temperature dependence of the relative intensities of the two EPR signals rules out macroscopic inhomogeneities and points toward a microscopic electronic phase separation. The qualitatively different behavior of the broad and narrow EPR signals indicates that they belong to distinct regions in the sample. First, we notice that the broad line vanishes at low temperatures. This can be explained by taking into account the AF order present in samples with very low Sr concentration [3]. Here one should recall that the coupled Mn-Cu system in LSCO experiences a strong bottleneck regime [8]. In the bottleneck regime, the collective motion of the total magnetic moment of the Mn and Cu spin system appears because the relaxation rate between the magnetic moments of the Mn and Cu ions is much faster than their relaxation rates to the lattice due to the strong isotropic Mn-Cu exchange interaction. It is expected that, upon approaching the AF ordering temperature, a strong shift of the resonance frequency and an increase of the relaxation rate of the Cu spin system will occur. This will break the bottleneck regime of the Mn^{2+} ions, and as a consequence the EPR signal becomes unobservable [5]. Because of the bottleneck opening, the linewidth of the broad signal will depend on the Mn-Cu relaxation rate. The temperature dependence of the latter is very sensitive to the doping, dimensionality, and the size of the

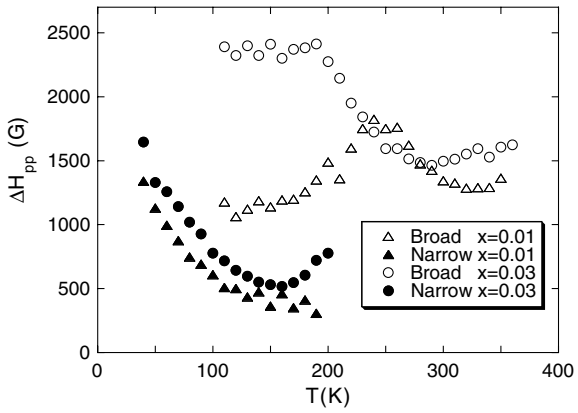

FIG. 2. Temperature dependence of the peak-to-peak linewidth ΔH_{pp} for the narrow and broad EPR lines in $La_{2-x}Sr_xCu_{0.98}Mn_{0.02}O_4$ with $x = 0.01$ and 0.03.

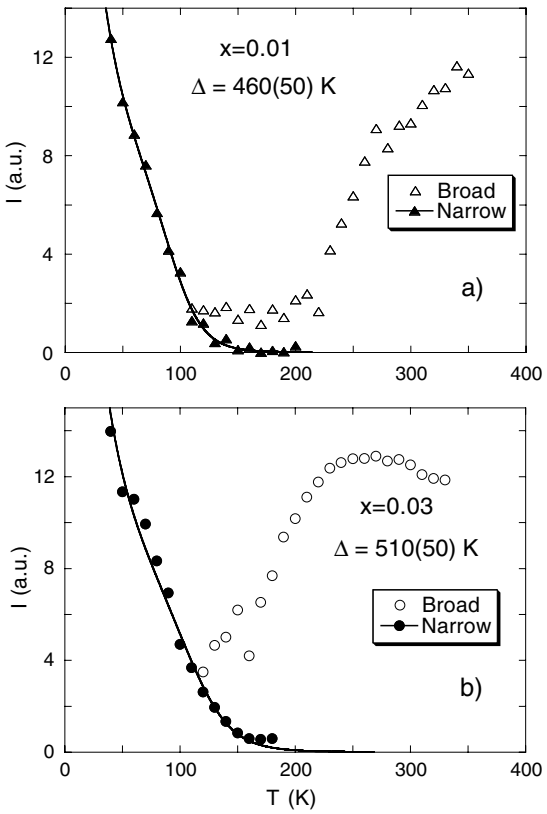

FIG. 3. Temperature dependence of the narrow and broad EPR signal intensity in $La_{2-x}Sr_xCu_{0.98}Mn_{0.02}O_4$ with different Sr dopings: (a) $x = 0.01$; (b) $x = 0.03$. The solid lines represent fits using the model described in the text.

hole-poor regions. This results in a complicated temperature dependence of the linewidth of the broad signal [5].

In contrast to the broad line, the narrow signal appears at low temperatures and its intensity increases with decreasing temperature. This indicates that the narrow signal is due to the regions without AF order. It is known that the AF order is destroyed by the doped holes, and above $x = 0.06$ AF fluctuations are much less pronounced [9]. Therefore, it is natural to relate the narrow line to regions with locally high carrier concentration and high mobility. This assumption is strongly supported by the absence of an oxygen isotope effect on the linewidth of the narrow line as well [6]. It was shown previously that the isotope effect on the linewidth decreases at high charge-carrier concentrations close to the optimum doping [5]. We obtain another important indication from the temperature dependence of the EPR intensity shown in Fig. 3. Because we relate the narrow line to hole-rich regions, an exponential increase of its intensity at low temperatures indicates an energy gap for the existence of these regions. This is the *main experimental observation* of the present Letter.

It is interesting to compare our results with other experiments performed in lightly doped LSCO. Recently Ando *et al.* measured the in-plane anisotropy of the resistivity ρ_b/ρ_a in single crystals of LSCO with $x = 0.02$–0.04 [4]. They found that at high temperatures the anisotropy is small, which is consistent with the weak orthorhombicity present. However, ρ_b/ρ_a grows rapidly with decreasing temperature below $\sim$150 K. This provides macroscopic evidence that electrons self-organize into an anisotropic state because there is no other external source to cause the in-plane anisotropy in $La_{2-x}Sr_xCuO_4$. With EPR being a real-space and local probe, it is difficult to determine the shape of the hole-rich regions. However, we noticed that the temperature dependence of the narrow EPR line intensity is very similar to that of ρ_b/ρ_a obtained by Ando *et al.* [see Fig. 2(d) in Ref. [4]].

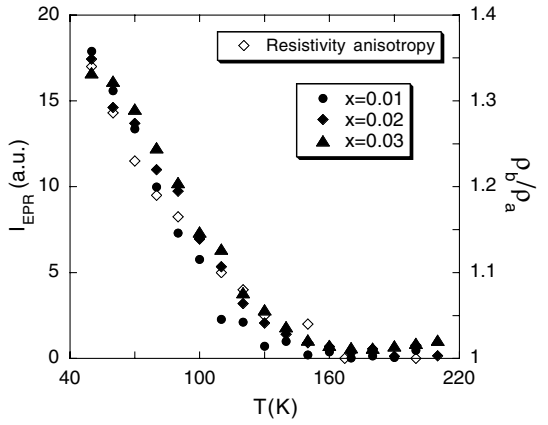

FIG. 4. Temperature dependence of the narrow EPR line intensities in $La_{2-x}Sr_xCu_{0.98}Mn_{0.02}O_4$ and of the resistivity anisotropy ratio in $La_{1.97}Sr_{0.03}CuO_4$ obtained in Ref. [4].

To make this similarity clear, we plotted $I_{\text{narrow}}(T)$ and $\rho_b/\rho_a(T)$ on the same graph (see Fig. 4). It is remarkable that both quantities show very similar temperature dependences. It means that our *microscopic* EPR measurements and the *macroscopic* resistivity measurements by Ando *et al.* provide evidence of the same phenomenon: the formation of hole-rich metallic stripes in lightly doped LSCO well below $x_{c1} = 0.06$. This conclusion is also supported by a recent angle-resolved photoemission study of LSCO which showed the existence of metallic quasiparticles near the nodal direction below $x = 0.06$ [10].

The mechanism of the stripe formation in cuprates is still under debate. Until now, the main attention was paid to the purely electronic and magnetic mechanisms of the stripe formation [11]. The existence of stripes within this approach is still controversial. We propose an alternative mechanism for the stripe formation. In the latter, the electron-phonon coupling induces anisotropic interactions between the holes resulting in the creation of extended nanoscale hole-rich regions.

It was shown that the interaction between charge carriers via the phonon exchange reduces to usual elastic forces if we neglect the retardation effects and optical modes [12]. In this case, the interaction between the holes is highly anisotropic, being attractive for some orientations and repulsive for others [13]. The attraction between holes may result in a pair formation, which can be a starting point for the creation of hole-rich regions by attracting of additional holes. Because of the highly anisotropic elastic forces, these regions are expected to have the form of stripes. Therefore the pair formation energy Δ can be considered as an energy gap for the formation of hole-rich regions.

The intensity of the narrow EPR line will be proportional to the product of the Curie-Weiss susceptibility of the bottlenecked Mn-Cu system and the volume of the sample occupied by the hole-rich regions. We expect that the volume in question is proportional to the number of hole pairs, which can be estimated in a way used by Mihailovic and Kabanov [7]. If the density of states is determined by $N(E) \sim E^{\alpha}$, the number of pairs is

$$N_{\text{pair}} = (\sqrt{z^2 + x} - z)^2, \qquad z = KT^{\alpha+1}e^{-(\Delta/T)}, \quad (1)$$

where Δ is the energy of pair formation, x is the level of hole doping, and K is a temperature- and doping-independent parameter related to the free polaron density of states. The intensity of the narrow EPR line will be

$$I_{\text{narrow}} \sim \frac{C}{T - \theta} N_{\text{pair}}, \quad (2)$$

where C is the Curie constant and θ is the Curie-Weiss temperature. The experimental points for the narrow line intensity were fitted for the two-dimensional system ($\alpha = 0$), and we used the value $\theta = -8$ K, which was

found from measurements of the static magnetic susceptibility (an attempt to vary θ yielded about the same value). The values of C and θ are determined mainly by the concentration and magnetic moment of the Mn ions and their coupling with the Cu ions. Since these parameters are expected to be doping independent (or weakly dependent), they were found by fitting for the sample $x = 0.01$ and then were kept constant for other concentrations leaving the only free parameter the energy gap Δ. The results of the fit are shown in Fig. 3(a) and 3(b). We obtained the pair formation energy $\Delta = 460(50)$ K, which is practically doping independent. This value is very close to $\Delta = 510$ K obtained from the analysis of inelastic neutron scattering and Raman data in cuprate superconductors [7]. Mihailovic and Kabanov identified the pairs as intersite Jahn-Teller pairs which may be called bipolarons [14].

Recently, Kochelaev *et al.* performed theoretical calculations of the polaron interactions via the phonon field using the extended Hubbard model [13]. They estimated the bipolaron formation energy and obtained values of $100\ \text{K} \leq \Delta \leq 730$ K, depending on the Coulomb repulsion between holes on neighboring copper and oxygen sites V_{pd}, $0 \leq V_{pd} \leq 1.2$ eV. We note also that recently Khomskii and Kugel emphasized an important role of the elastic interactions for stripe formation in doped manganates [15].

Finally, we would like to comment on the observability of the phase separation in our EPR experiments. The main difference of the EPR signals from the hole-rich and hole-poor regions is the spin relaxation rate of the Cu spin system, which results in different EPR linewidths. One would expect these local differences of the relaxation rate to be averaged out by the spin diffusion. The spin diffusion in the CuO_2 plane is expected to be very fast because of the huge exchange integral between the Cu ions. A rough estimate shows that during the Larmor period a local spin temperature can be transported over 100 Cu-Cu distances. It means that all the different nanoscale regions will relax to the lattice with a single relaxation rate, and we cannot distinguish them with EPR. However, the AF order which appears below T_N in the hole-poor regions in lightly doped LSCO freezes the process of spin diffusion, and makes it possible to see distinct EPR lines from the two types of regions. We expect that with increasing doping, where magnetic order gets suppressed, spin diffusion will become faster, extended, and we can no longer distinguish different regions with EPR. This is most probably what happens in samples with $x \geq 0.06$, where only a single EPR line is observed [5]. The phase separation in hole-rich and hole-poor regions probably also exists at $x \geq 0.06$, but the spin diffusion averages out the EPR response from these regions. In fact, recent Raman and infrared measurements provided evidence of one-dimensional conductivity in LSCO with $x = 0.10$ [16].

In summary, EPR measurements in lightly doped LSCO revealed the presence of two resonance signals: a narrow one and a broad one. Their behavior indicates that the narrow signal is due to hole-rich metallic regions and the broad signal due to hole-poor AF regions. The narrow line intensity is small at high temperatures and increases exponentially below ~150 K. The activation energy inferred, $\Delta = 460(50)$ K, is nearly the same as that deduced from other experiments for the formation of bipolarons, pointing to the origin of the metallic stripes present. We found a remarkable similarity between the temperature dependences of the narrow line intensity and recently measured resistivity anisotropy in CuO_2 planes in lightly doped LSCO [4]. *The results obtained provide the first magnetic resonance evidence of the formation of hole-rich metallic domains in lightly doped LSCO well below* $x_{c1} = 0.06$. Furthermore, they also lend support to the recently proposed model of phase coherence by percolation [17], in which the macroscopic phase coherence in superconducting cuprates is determined by random percolation between mesoscopic pairs, stripes, or clusters.

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