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LETTER TO THE EDITOR

The ratio of small polarons to free carriers in $La_{2-x}Sr_xCuO_4$ derived from susceptibility measurements

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Abstract. The normal-state spin susceptibility χ of $La_{2-x}Sr_xCuO_4$ was measured as a function of doping x. For $x \leqslant x_t = 0.09$, χ is well described by small-polaron theory. For $x \geqslant x_t$, a temperature-independent Pauli component is present in χ as well. These results indicate the coexistence of small polarons and free carriers above the transition concentration x_t. The concentration of the free carriers increases rapidly with $x - x_t$, reaching a maximum for optimal doping ($x = 0.15$). The large mass anisotropy of the polarons is obtained quantitatively from the χ-measurements.

Since the first suggestion by Landau in 1933, the research on polarons has grown to a vast field of research. Carriers in polar crystals can distort their environment over many lattice distances. They are called large polarons. These contrast with polarons for which the excess carriers cause only a local displacement of nearest neighbours, called small polarons. The origin can again be polar, but it can also be molecular. Among those with the latter origin, Jahn–Teller (JT) polarons were proposed by a theoretical group in Basel [1]. Their existence causes the giant $^{16}O/^{18}O$ oxygen isotope effect observed macroscopically in the ferromagnetic transition temperature in $La_{1-x}Ca_xMnO_{3+y}$ [2], and microscopically in the electron paramagnetic resonance (EPR) linewidths [3]. Recently the existence of JT polarons in rare-earth nickelates was also inferred quantitatively from structure analyses and oxygen isotope effects [4]. In the JT effect the Born–Oppenheimer approximation, i.e. the decoupling of nuclear and electronic motion, breaks down. The concept of JT polarons—which do not need to be small ones—led to the discovery of the copper oxide superconductors [5]. Most recent research indicates that in several copper oxides large polarons, i.e. free-carrier-type ones, and small polarons coexist [6], as was deduced much earlier to be the case for the oxides WO_{3-x} [7] and $NbO_{2.5-x}$ [8]. In the cuprates the small polarons are indeed of the Q_2-variety as inferred from EXAFS, NMR, and optical pulse experiments [6] as well as most recently by means of EPR [9]. On the other hand, in $La_{1-x}Ca_xMnO_3$ they are of the Q_3-type [10]. In this work new high-precision susceptibility measurements for $La_{2-x}Sr_xCuO_4$ are presented and complemented with earlier ones obtained by Johnston [11]; from our set of results the ratio of large to small polarons is deduced. This was made possible by assuming that a Pauli spin susceptibility applies for the former and that the latter obey formulae derived recently by Alexandrov, Kabanov and Mott (AKM) [12]. The outcome shows that, upon doping, at first only small polarons are formed until a threshold is reached where free carriers are also present with increasing density, as is the case for WO_{3-x}, $NbO_{2.5-x}$ and other oxides.

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Samples of $La_{2-x}Sr_xCuO_4$ were prepared by a conventional solid-state reaction using dried La_2O_3 (99.99% pure), $SrCO_3$ (99.999% pure) and CuO (99.999% pure). The powders were mixed, ground thoroughly, pressed into pellets and fired in air at 1000 °C for ∼96 h with three intermediate grindings. Then they were annealed in air at 900 °C for 12 h and under 1 bar of oxygen at 900 °C for 40 h, then cooled to room temperature in 4 h. The magnetization was measured in a magnetic field of 2 T with a Quantum Design SQUID magnetometer. The background due to the sample holder is small (∼5–10% of the sample signal) and has been subtracted from all of the data shown.

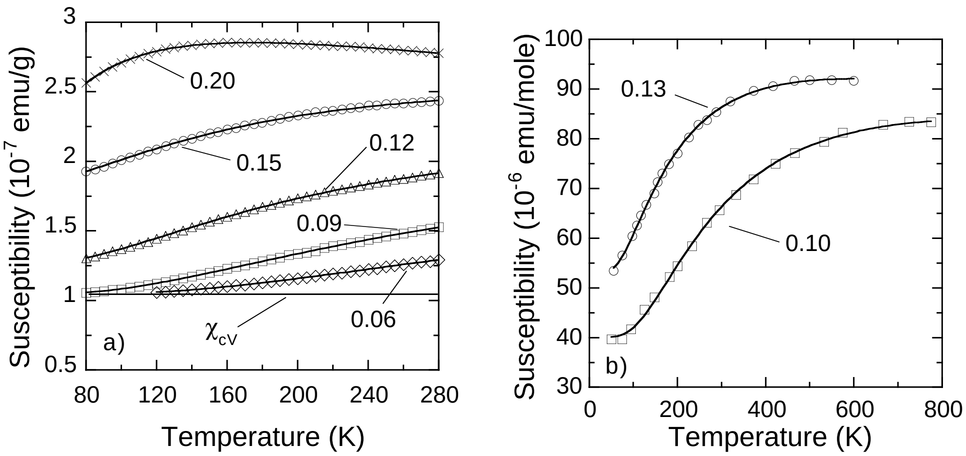

Figure 1. (a) Temperature dependences of the normal-state susceptibility for $La_{2-x}Sr_xCuO_4$. The horizontal line marks the contributions from the core diamagnetic and Van Vleck paramagnetic susceptibility. (b) The normal-state susceptibility for $La_{2-x}Sr_xCuO_4$ taken from Johnston [11]. The solid lines represent the fitting curves obtained using equation (2).

Figure 1(a) shows the temperature dependence of the normal-state susceptibility for $La_{2-x}Sr_xCuO_4$ for $x = 0.06$, 0.09, 0.12, 0.15, 0.20. The results below 80 K are omitted to avoid the effects of diamagnetism due to superconducting fluctuations, and of paramagnetism from solid oxygen due to a possible nonzero oxygen contamination in the sample chamber. For $x = 0.20$, a small Curie paramagnetic susceptibility has been subtracted. Our data are consistent with those reported in reference [11], shown in figure 1(b) for comparison. For $x = 0.06$, there is an additional contribution in the susceptibility below about 100 K (not shown) due to the antisymmetric AFM exchange interaction in the orthorhombic structure [13]. The sum of the contributions from the core diamagnetic and Van Vleck paramagnetic susceptibility $\chi_{cV} = \chi_c + \chi_V$ is also indicated in figure 1(a). The magnitude of χ_{cV} is about $1.05(5) \times 10^{-7}$ emu g^{-1}, as determined from the ^{63}Cu Knight shift of $La_{2-x}Sr_xCuO_4$ (reference [14]). From the ^{17}O Knight shift of $La_{1.85}Sr_{0.15}CuO_4$ with the hyperfine coupling constant 130 kOe/μ_B [15], one can extract a spin susceptibility of $\sim 1.0 \times 10^{-7}$ emu g^{-1} at 100 K for $La_{1.85}Sr_{0.15}CuO_4$, in excellent agreement with our data. Therefore, the present estimate of χ_{cV} is quite reliable.

AKM [12] discussed the normal-state susceptibility data for $La_{2-x}Sr_xCuO_4$ reported by Nakano *et al* [13] on the basis of their small-(bi)polaron theory. This theory predicts a temperature-dependent spin susceptibility

$$\chi_{AKM}(T) = B_\infty T^{-1/2} \exp(-\Delta/2T). \tag{1}$$

Here $B_\infty \propto x^{1/2}(m^*/m^{**}_{ab})^{1/2}$, where $m^* \simeq m^*_c$ is the effective *single-polaron* mass, m^{**}_{ab} is the effective in-plane *bipolaron* mass, x is the Sr content and Δ is the bipolaron binding energy. Note that m^{**}_{ab} is of the same order as m^*_{ab} ($m^{**}_{ab} \approx m^*_{ab}$), but the effective bipolaron mass along the c-axis, m^{**}_c, is strongly enhanced ($m^{**}_c/m^*_c \gg 1$) [12]. Analysing the susceptibility data of reference [13] in terms of equation (1), AKM found that the bipolaron binding energy Δ strongly depends on the temperature, which is not in agreement with their own theoretical prediction.

Recent experimental investigations of the mesoscopic structure of cuprate superconductors by x-ray absorption (EXAFS), neutron scattering and other techniques have provided increasing evidence of charge ordering in the inhomogeneous CuO_2 plane, giving rise to a superlattice of alternating quantum stripes in the CuO_2 plane with an approximate width of 10 Å [16]. If one considers there to be two different kinds of charge carrier present in the alternating stripes, i.e., small-(bi)polaronic-type carriers in stripes A and Fermi-liquid-type carriers in adjacent stripes B [6, 17], one may be able to explain the spin susceptibility data very well, as will be shown here. The stripe phase may be dynamic, but this will not affect the total spin susceptibility which is the average of the susceptibilities of stripe phases A and B.

For small-(bi)polaronic charge carriers, the spin susceptibility is given by $\chi_{AKM}(T)$ defined in equation (1), whereas the Fermi-liquid charge carriers give rise to a temperature-independent susceptibility χ_F. So the total susceptibility for the two-component stripe-phase system is

$$\chi(T) = f_s\chi_{AKM}(T) + (1 - f_s)\chi_F + \chi_{cV} \equiv f_s\chi_{AKM}(T) + \chi_0$$

where f_s is the fraction of small-(bi)polaronic carriers. Then

$$\chi(T) = f_s B_\infty T^{-1/2}\exp(-\Delta/2T) + \chi_0. \qquad (2)$$

The solid lines in figure 1 represent the fitting curves obtained using equation (2). One can see that the fitting is excellent for all of the compositions.

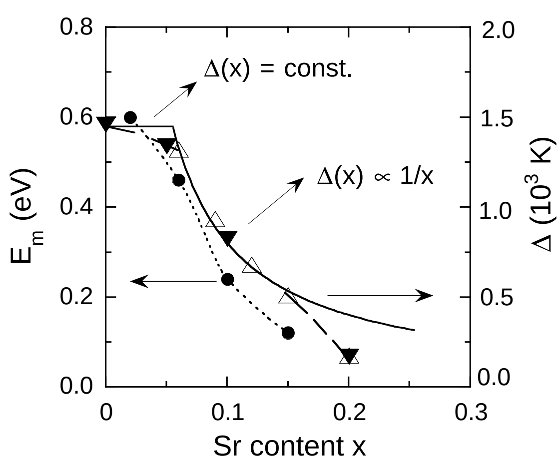

Figure 2. Composition dependences of the bipolaron binding energy Δ and $E_m \equiv 2g^2\hbar\omega$. The left-hand and right-hand scales are for the circle and triangle symbols, respectively. The solid triangles represent T_{max} as determined by Johnston [11]. Δ is proportional to $1/x$ for $0.06 \leqslant x \leqslant 0.15$. The results for E_m are from reference [18].

Figure 2 shows the composition dependences of the bipolaron binding energy Δ, and $E_m \equiv 2g^2\hbar\omega$. Here E_m is an energy corresponding to the maximum ac conductivity in the mid-infrared region [18], ω is the characteristic longitudinal optical phonon frequency and g^2 is related to the polaron mass enhancement factor $\exp(g^2)$. The solid triangles represent T_{max} as measured by Johnston [11]. Since $T_{max} = \Delta$ according to equation (2), the measured values of T_{max} should be consistent with our deduced values of Δ if the susceptibility data can be exactly fitted by equation (2) over the temperature region investigated. The consistency, as seen from figure 2, gives an independent check for the validity of our data analysis. From the figure, one can also see that Δ is proportional to $1/x$ for $0.06 \leqslant x \leqslant 0.15$. This is just as expected from the AKM theory if the local carrier density of the small (bi)polarons in the stripe domains A is proportional to x, in accordance with the proposed stripe-phase model [16] discussed above. The $1/x$ dependence of Δ was deduced earlier from mid-infrared absorption measurements [18] and most recently from photoinduced femtosecond transient optical transmission in underdoped $YBa_2Cu_3O_{7-\delta}$ [19]. AKM theory also predicts that below $x = 0.05$, Δ is nearly doping independent, and above the optimal doping ($x = 0.15$), Δ decreases much more quickly. All of these predictions are consistent with our experimental results shown in figure 2.

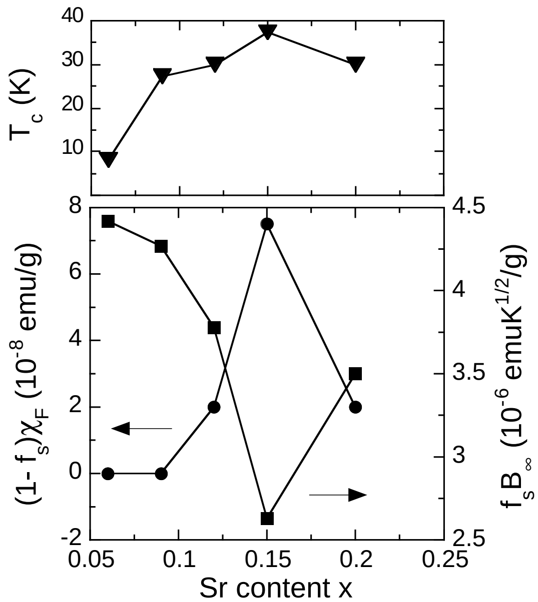

Figure 3. The composition dependences of T_c, $f_s B_\infty$ and $(1 - f_s)\chi_F$. $(1 - f_s)\chi_F$ has a maximum while $f_s B_\infty$ has a minimum at $x = 0.15$, where T_c is at its highest in this system.

In figure 3, we plot T_c, $f_s B_\infty$ and $(1 - f_s)\chi_F$ as functions of x. For $x \leqslant 0.09$, neither $f_s B_\infty$ nor $(1 - f_s)\chi_F$ depends on x, and $(1 - f_s)\chi_F$ is negligible. This implies that nearly all of the charge carriers are small (bi)polarons in this region, i.e., $f_s \approx 1$. The deduced $B_\infty = 4.4 \times 10^{-6}$ emu $K^{1/2}$ g^{-1} is very close to the theoretical estimate (5.5×10^{-6} emu $K^{1/2}$ g^{-1}) [12]. We also note that $(1 - f_s)\chi_F$ has a maximum while $f_s B_\infty$ has a minimum at $x = 0.15$ where T_c is at its highest in this system. Since B_∞ is nearly doping independent, and χ_F should be constant as a function of temperature for a 2D system, the above result implies that there is a minimum percentage of small (bi)polarons at the optimal doping, in good agreement with the x-ray diffuse scattering experiment which showed a minimum density of small (bi)polarons at the optimal doping [20]. From the values of $f_s B_\infty$, we can estimate f_s to be 0.85, 0.60, 0.80 for $x = 0.12$, 0.15 and 0.20, respectively. For $x = 0.15$, f_s has recently been determined to be about 0.5 from several independent experiments [21], in accord with our result here.

Our results thus show that small-(bi)polaronic and Fermi-liquid charge carriers coexist, and that the spin susceptibility arising from the small-(bi)polaronic charge carriers is in excellent agreement with the AKM theory. Since nearly all of the charge carriers are small (bi)polarons for $x \leqslant x_t = 0.09$, one should be able to calculate other physical properties using the AKM theory [22], especially superconducting quantities, such as the magnetic penetration depth and the supercarrier mass anisotropy, provided that the (bi)polaronic charge carriers condense into Cooper pairs in the superconducting state. This is indeed the case, as demonstrated recently by the observation of an oxygen isotope effect on the magnetic penetration depth in $La_{2-x}Sr_xCuO_4$ by our group [23]. For instance, using the expressions for the effective hopping integrals [12, 24] along and perpendicular to the CuO_2 plane, the effective supercarrier mass anisotropy $\gamma^2 = m_c^{**}/m_{ab}^{**}$ is readily obtained [22]:

$$\gamma^2 \propto \sqrt{\frac{\hbar\omega\Delta}{2\pi}}\exp\left[\frac{\Delta}{\hbar\omega}\left(1 + \ln\frac{E_m}{\Delta}\right)\right].$$

Note that γ strongly depends on the bipolaron binding energy Δ. As an example, using this formula Zhao *et al* [22] obtained $\gamma = 40$ for $x = 0.09$, in good agreement with the measured value of 56 for $x = 0.08$ (reference [25]). Recently, Hofer *et al* [26] used this formula to fit their measured doping dependence of γ for another one-layer cuprate superconductor, $HgBa_2CuO_{4+y}$, and obtained excellent agreement.

In summary, our experimental results show that small-(bi)polaronic and Fermi-liquid charge carriers coexist in the cuprate superconductor $La_{2-x}Sr_xCuO_4$. Nearly all of the charge carriers are small (bi)polarons for $x \leqslant 0.09$, and above $x_t = 0.09$ the carrier density of the Fermi-liquid-type ones increases rapidly. This behaviour is thus very similar to that exhibited by other oxides, first deduced for WO_{3-x} [7] and $NbO_{2.5-x}$ [8], in which an Anderson transition occurs as well. The normal-state gap in $La_{2-x}Sr_xCuO_4$ originates from the formation of small bipolarons, which are also formed in WO_{3-x} [7]. Furthermore, in the latter oxide the polarons are due to electrons and in the cuprates they are due to holes. The very large supercarrier mass anisotropy was shown to be in quantitative agreement with that predicted theoretically by AKM and from the present results. At optimal doping ($x = 0.15$), therefore, high-T_c superconductivity should arise from the coexistence of small-(bi)polaronic ($\sim$60%) and Fermi-liquid-type carriers ($\sim$40%), a consequence of the mesoscopic stripe structure in the CuO_2 observed in these materials.

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References

[1] Höck K-H, Nikisch H and Thomas H 1983 *Helv. Phys. Acta* **56** 237

[2] Zhao G M, Conder K, Keller H and Müller K A 1996 *Nature* **381** 676
Zhao G M, Hunt M B and Keller H 1997 *Phys. Rev. Lett.* **78** 955

[3] Shengelaya A, Zhao G M, Keller H and Müller K A 1996 *Phys. Rev. Lett.* **77** 5296

[4] Medarde M, Lacorre P, Conder K, Fauth F and Furrer A 1998 *Phys. Rev. Lett.* **80** 2397

[5] Bednorz J G and Müller K A 1986 *Z. Phys.* B **64** 189

[6] For a review, see
Mihailovic D and Müller K A 1997 *High-T_c Superconductivity 1996: Ten Years after the Discovery (NATO ASI Series E: Applied Sciences, vol 343)* ed E Kaldis, E Liarokapis and K A Müller (Dordrecht: Kluwer) p 243

[7] Salje E and Güttler B 1984 *Phil. Mag.* B **50** 607

[8] Rüscher C, Salje E and Hussain A 1988 *J. Phys. C: Solid State Phys.* **21** 3737
[9] Kochelaev B I, Sichelschmidt J, Elschner B, Lemor W and Loidl A 1997 *Phys. Rev. Lett.* **79** 4274
[10] Radaelli P G, Cox D E, Marezio M and Cheong S-W 1997 *Phys. Rev.* B **55** 3015
[11] Johnston D C 1989 *Phys. Rev. Lett.* **62** 957
[12] Alexandrov A S, Kabanov V V and Mott N F 1996 *Phys. Rev. Lett.* **77** 4796
[13] Nakano T, Oda M, Manabe C, Momono N, Miura Y and Ido M 1994 *Phys. Rev.* B **49** 16 000
[14] Song Y-Q, Kennard M A, Poeppelmeier K R and Halperin W P 1993 *Phys. Rev. Lett.* **70** 3131
[15] Ishida K, Kitaoka Y, Zheng G Q and Asayama K 1991 *J. Phys. Soc. Japan* **60** 3516
[16] For a review, see
Bianconi A, Saini N L, Lanzara A, Perali A, Rossetti T and Valletta A 1997 *High-T_c Superconductivity 1996: Ten Years after the Discovery (NATO ASI Series E: Applied Sciences, vol 343)* ed E Kaldis, E Liarokapis and K A Müller (Dordrecht: Kluwer) p 383
[17] Mihailovic D, Mertelj T and Müller K A 1998 *Phys. Rev.* B **57** 6116
[18] Bi X X and Eklund P C 1993 *Phys. Rev. Lett.* **70** 2625
[19] Kabanov V V, Demsar J, Podobnik B and Mihailovic D 1998 *Preprint*
[20] Dmowski W, McQueeney R J, Egami T, Feng Y P, Sinha S K, Hinatsu T and Uchida S 1995 *Phys. Rev.* B **52** 6829
[21] Dolgov O V, Kaufmann H J, Salje E K H and Yagil Y 1997 *Physica* C **279** 113
[22] Zhao G M, Conder K, Keller H and Müller K A 1998 in preparation
[23] Zhao G M, Hunt M B, Keller H and Müller K A 1997 *Nature* **385** 236
[24] Alexandrov A S 1996 *Phys. Rev.* B **53** 2863
[25] Suzuki M and Hikita M 1995 *Phys. Rev. Lett.* **75** 4662
[26] Hofer J, Karpinski J, Willemin M, Meijer G I, Kopnin E M, Molinski R, Schwer H, Rossel C and Keller H 1998 *Physica* C **297** 103