Theoretical exploration of electronic structure in cuprates from electronic entropy

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(Received 10 July 2001; revised manuscript received 27 March 2002; published 2 August 2002)

The electronic entropy of superconducting cuprates includes crucial information on the metallic state. In this context the electronic entropy of cuprates is calculated for the CuO_2 layer in order to clarify the features of metallic states. It is shown that the observed peculiar doping dependence of electronic entropy can be explained by the Kamimura-Suwa model without introducing the pseudogap concept, while an ordinary band structure gives too small values even in the overdoped region. It is also shown that the observed anomalous behaviors in normal-state properties of cuprates such as resistivity and the Hall effect are explained by the Kamimura-Suwa model. From these results it is suggested that the hole carriers in cuprates form a metallic state by taking the Zhang-Rice singlet and Hund's coupling triplet alternately in the presence of the local antiferromagnetic ordering.

DOI: 10.1103/PhysRevB.66.054504 PACS number(s): 74.25.Jb, 74.62.Dh

I. INTRODUCTION

Since Bednorz and Müller[1] discovered high-temperature superconductivity in $La_{2-x}Ba_xCuO_4$, a number of theoretical models have been proposed. Among them Anderson[2] was the first to point out the important role of strong correlation in this system of materials. However, the exact solution that takes into account the various many-body interactions still eludes us today. Most of the proposed models start by assuming an electronic structure of the copper oxide followed by a refinement which makes use of disposable parameters to fit experimental data.[3] This procedure makes it difficult to assess the predictive nature of the model, for example, how cuprates containing CuO_6 octahedra or CuO_5 pyramids may give rise to different features of high-T_c superconductivity. In an attempt to address this problem, Kamimura and coworkers have carried out a series of theoretical studies beginning with the calculations of the electronic structure of $La_{2-x}Sr_xCuO_4$ (hereafter abbreviated as LSCO) from first principles by Kamimura and Eto.[4,5] Unlike the usual approach of modifying the Fermi liquid picture by treating cuprates already in a highly doped state, their calculations began by considering the electronic structure of the lightly doped superconductors. The theoretical treatments by Kamimura and Eto[4,5] are based on embedding a hole-doped single CuO_6 octahedron in LSCO structure and employing a multiconfiguration self-consistent field variational method with configuration interaction (MCSCF-CI). The MCSCF-CI method is the most suitable variational method to calculate the electronic structure of a strongly correlated cluster system. Recently Kamimura and Sano[6] and Tobita and Kamimura[7] have extended these calculations to include those of a single CuO_5 pyramid embedded in $YBa_2Cu_3O_7$ (abbreviated as $YBCO_7$) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (abbreviated as Bi2212), respectively.

Based on the first-principles cluster calculations for a CuO_6 octahedron embedded in LSCO by Kamimura and Eto,[4,5] Kamimura and Suwa[8] constructed a metallic state of underdoped cuprates by introducing the transfer interactions between the neighboring CuO_6 octahedra, where they assumed that the localized spins in the CuO_2 layer form antiferromagnetic (AF) ordering by the superexchange interaction in an area whose length is the magnitude of a spin-correlation length. In this metallic state the dopant holes can move relatively freely in the CuO_2 plane by taking the character of a Zhang-Rice spin-singlet state and that of a Hund's-coupling spin-triplet state alternately between neighboring sites. This carrier motion does not disturb the underlying AF ordering and can lead to superconductivity of *d*-wave pairing symmetry.[9] This model is called the ''Kamimura-Suwa (KS) model.'' An important consequence of the KS model is that, having taken into account the strong spin-exchange interactions between the spins of a dopant hole and a localized hole at the same site in a mean-field approximation, the thermal and transport properties of the highly underdoped cuprates can be treated within a framework similar to a single-particle band structure. The systems of $YBCO_7$ and Bi2212 can also have a similar kind of electronic states according to Refs. 6 and 7.

Recently, phenomena which can be attributed to the reduction of the density of states near the Fermi energy, called the *pseudogap*, have been observed.[10] A striking example that has drawn considerable attention is the strange doping dependence of the electronic entropy in LSCO observed by Loram *et al.*[10] Since the electronic entropy depends on the density of states of hole carriers, it includes crucial information on the metallic state of cuprates. In this context, we will calculate the electronic entropy by using two kinds of the density of states of hole carriers in cuprates obtained by first-principles calculations. Those are the density of states calculated by the KS model on the one hand and that calculated by the ordinary band theory with the local density approximation (LDA) on the other.

In this paper, we will show that this peculiar doping dependence of the electronic entropy can be explained by the KS model[8] without any adjustable parameters, while the

LDA band structure gives too small values even in the overdoped region, compared with the experimental values. This means that the metallic state of cuprates may be described by the KS model. In order to show further experimental supports for the KS model, in this paper we will also calculate the normal-state transport properties of LSCO based on the KS model, such as the temperature and hole-concentration dependences of the resistivity and of the Hall coefficient, and compare the calculated results with experimental ones.

In Sec. II we describe the KS model briefly. In Sec. III the calculated results of the electronic entropy for LSCO are presented and compared with experimental results. In Sec. IV we describe the structure of Fermi surface based on the KS model. In Sec. V the calculated results of the resistivity and of the Hall coefficient for LSCO are presented and compared with experiments. Finally a summary is given in Sec. VI.

II. KAMIMURA-SUWA MODEL

A. Introduction

In this section, we will describe briefly the theoretical treatment of the KS model[8] and its physical justification. In the presence of AF order, a pair of neighboring CuO_6 octahedra (or CuO_5 pyramids) with their up and down localized spins are to be taken as a basis unit, where the localized holes occupy the antibonding b_{1g} (b_1) orbital, b_{1g}^* (b_1^*), with a main character of Cu $d_{x^2-y^2}$ orbital. Consider a dopant hole with an up spin within this basis unit. It can either occupy the antibonding a_{1g} (a_1) orbital a_{1g}^* (a_1^*) in the up-spin half of the octahedron (pyramid) pair and form a spin-triplet state with a localized up spin via Hund's coupling or the bonding b_{1g} (b_1) orbital in the neighboring CuO_6 octahedron (CuO_5 pyramid) with a localized down spin and form a spin-singlet state as shown in Fig. 1(a), where the a_{1g}^* (a_1^*) orbital consists of a Cu d_{z^2} orbital and surrounding six (five) oxygen p orbitals while the b_{1g} (b_1) orbital consists mainly of the four in-plane oxygen p_σ orbitals hybridized by the Cu $d_{x^2-y^2}$ orbital. According to the first-principles cluster calculations for a CuO_6 octahedron in LSCO by Kamimura and Eto,[4,5] for a CuO_5 pyramid in $YBCO_7$ by Kamimura and Sano,[6] and for a CuO_5 pyramid in Bi2212 by Tobita and Kamimura,[7] the energy separation between the Hund's coupling triplet multiplet denoted by $^3B_{1g}$ (or $^3B_1$) and the Zhang-Rice singlet multiplet denoted by $^1A_{1g}$ (or $^1A_1$) in a CuO_6 octahedron (or a CuO_5 pyramid) is about 0.1 eV, where a multiplet means a many-electron eigenstate in a single CuO_6 octahedron cluster or a CuO_5 pyramid cluster. This value is of the same order as the transfer interaction energy (~ 0.3 eV) between nearest-neighbor sites, after taking into account the observed local distortion of the CuO_6 octahedron (CuO_5 pyramid.)[11,12] Thus, in the KS model, the dopant holes can move coherently from one CuO_6 octahedron (CuO_5 pyramid) to a neighboring CuO_6 octahedron (CuO_5 pyramid) in a CuO_2 layer by the transfer interaction, assisted by localized AF order but without disturbing this order.[13] The situation for a down-spin hole is energetically similar but occupies a complementary electronic configuration as shown in Fig. 1(b). This characteristic feature in the wave functions of dopant up- and down-spin holes is the origin for the d-wave symmetry of a Cooper pair.[9]

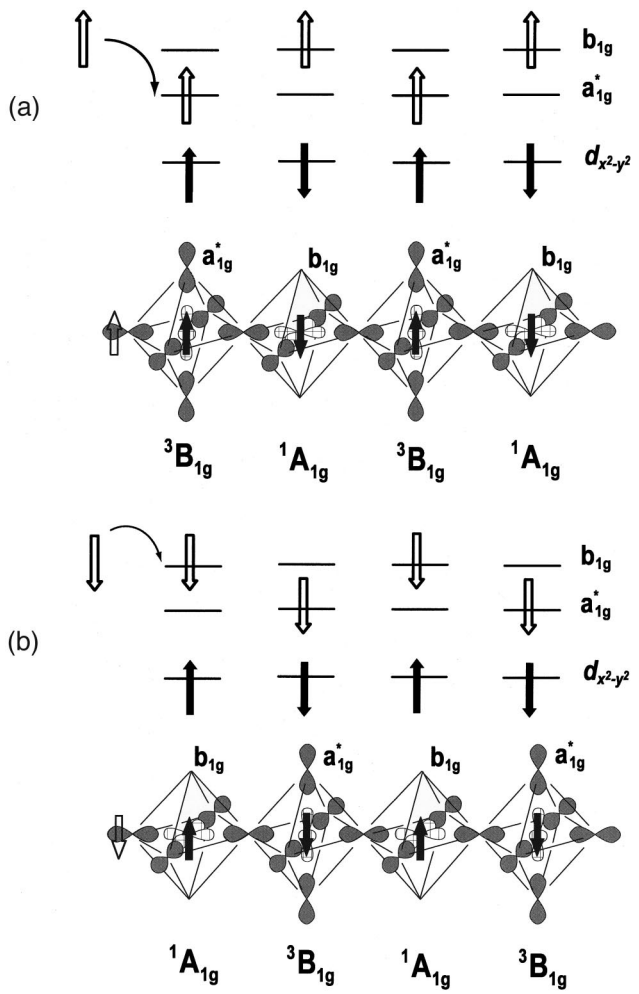

FIG. 1. Schematic view of the coherent motion of a dopant hole from the Hund's coupling triplet state to the Zhang-Rice singlet state and then to the Hund's coupling triplet state, etc., in the presence of AF ordering of the localized spin system in the case of superconducting LSCO. Here (a) and (b) correspond to states for up spin and down spin of a dopant hole, respectively, where the white arrow represents the spin of a dopant hole while the black arrow represents the spin of a localized hole which forms AF order via superexchange interaction.

The coexistence of the character of the Hund's coupling triplet and Zhang-Rice singlet states has been experimentally verified by Chen *et al.*[14] and Pellegin *et al.*[15] In order to check the character of the Hund's coupling triplet state, they performed polarization-dependent x-ray absorption measurements for O K and Cu L edges in LSCO. As for Cu L edges, they observed the doping-induced satellite peak (L_3') for both polarizations of the electric vector of the x ray, $\boldsymbol{E}$, parallel and perpendicular to the c axis, in a shoulder area of the doping-independent Cu L_3 line, where the L_3 line corresponds to transitions from the Cu $2p$ core level to the upper Hubbard Cu $d_{x^2-y^2}$ band. Since the former $(\boldsymbol{E} \| c)$ and the latter $(\boldsymbol{E} \perp c)$ polarizations detect the characters of the

Hund's coupling triplet state and of the Zhang-Rice singlet state, respectively, the appearance of the doping-induced satellite peak for both polarizations *at the same energy* suggested that a state of dopant holes must consist of the Hund's coupling triplet state and the Zhang-Rice singlet state. In addition, recent site-specific x-ray absorption spectroscopy by Merz *et al.*[16] has given clear evidence for the prominent role of apical oxygen in the metallic state of cuprates. According to their result the experimental values of the hole distribution in a CuO_2 plane, at an apical O site and in a Cu-O chain, are 0.4, 0.27, and 0.24, respectively, for superconducting $YBa_2CuO_{6.91}$, while vanishing for insulating $Y_{0.97}Ca_{0.03}Ba_2Cu_3O_{6.0}$. Since the a_{1g}^* (a_1^*) orbital in the Hund's coupling triplet state contains the p_z orbital at an apical oxygen site, the experimental results by Merz *et al.*[16] may be considered as clear experimental support for the KS model.

B. Effective Hamiltonian for the Kamimura-Suwa model

The following effective Hamiltonian is introduced in order to describe the KS model.[8] It consists of four parts: the effective one-electron Hamiltonian $H_{\rm eff}$ for $a_{1g}^*(a_1^*)$ and $b_{1g}(b_1)$ orbital states; the transfer interaction between neighboring CuO_6 octahedra (CuO_5 pyramids), $H_{\rm tr}$, the superexchange interaction between the Cu $d_{x^2-y^2}$ localized spins, $H_{\rm AF}$; and the exchange interactions between the spins of dopant holes and $d_{x^2-y^2}$ localized holes within the same CuO_6 octahedron (CuO_5 pyramid), $H_{\rm ex}$. Thus we have

$$\begin{aligned} H &= H_{\rm eff}+H_{\rm tr}+H_{\rm AF}+H_{\rm ex} \\ &= \sum_{i,m,\sigma} \varepsilon_m C_{im\sigma}^{\dagger} C_{im\sigma} \\ &\quad - \sum_{\langle i,j\rangle,m,n,\sigma} t_{mn}(C_{im\sigma}^{\dagger} C_{jn\sigma}+\text{H.c.}) + J\sum_{\langle i,j\rangle} \boldsymbol{S}_i\cdot\boldsymbol{S}_j \\ &\quad + \sum_{i,m} K_m \boldsymbol{s}_{i,m}\cdot\boldsymbol{S}_i , \end{aligned} \tag{1}$$

where ε_m [$m=a_{1g}^*(a_1^*)$ or $b_{1g}(b_1)$] represents the effective one-electron energy of the $a_{1g}^*(a_1^*)$ and $b_{1g}(b_1)$ orbital states, $C_{im\sigma}^{\dagger}$ and $C_{im\sigma}$ are the creation and annihilation operators of a dopant hole with spin σ in the ith CuO_6 octahedron (ith CuO_5 pyramid), respectively, t_{mn} the effective transfer integrals of a dopant hole between m-type and n-type orbitals of neighboring CuO_6 octahedra (CuO_5 pyramids), J the superexchange interaction between the spins $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ of $d_{x^2-y^2}$ localized holes in the $b_{1g}^*(b_1^*)$ orbital at the nearest-neighbor Cu sites i and j ($J>0$ for AF interaction), and K_m the exchange integral for the exchange interaction between the spin of a dopant hole $\boldsymbol{s}_{im}$ and the $d_{x^2-y^2}$ localized spin $\boldsymbol{S}_i$ in the ith CuO_6 octahedron (ith CuO_5 pyramid).

The values of the parameters in Eq. (1) are $J=0.1$, $K_{a_{1g}^*}=-2.0$, $K_{b_{1g}}=4.0$, $t_{a_{1g}^*a_{1g}^*}=0.2$, $t_{b_{1g}b_{1g}}=0.4$, $t_{a_{1g}^*b_{1g}}=\sqrt{t_{a_{1g}^*a_{1g}^*}t_{b_{1g}b_{1g}}}\sim 0.28$, $\varepsilon_{a_{1g}^*}=0$, $\varepsilon_{b_{1g}}=2.6$ in units of eV, where the values of Hund's coupling exchange constant $K_{a_{1g}^*}$ and Zhang-Rice exchange constant $K_{b_{1g}}$ are taken from the first-principles cluster calculations for a CuO_6 octahedron in LSCO,[4] and the energy difference of the effective one-electron energies between a_{1g}^* and b_{1g} orbital states, $\varepsilon_{a_{1g}^*}-\varepsilon_{b_{1g}}=-2.6$, is determined so as to reproduce the energy difference between the $^3B_{1g}$ and $^1A_{1g}$ multiplets in LSCO in the MCSCF cluster calculations,[5] while those of t_{mn}'s are due to band structure calculations.[17–19]

C. Derivation of an effective one-electron type energy band

In order to solve the effective Hamiltonian (1), Kamimura and Ushio[20] paid attention to the experimental results by Mason *et al.*,[21] Yamada *et al.*,[22] and Lee *et al.*[23] that the spin-correlation length λ_s in the underdoped region of LSCO increases as the Sr concentration increases from $x=0.05$, the onset of superconductivity, and reaches a value of about 50 Å or more at optimum doping ($x=0.15$). In this spin-correlated region, the frustrated spins on its boundary change their directions by the fluctuation effect in the two-dimensional (2D) Heisenberg AF spin system during the time of τ_s defined by $\tau_s\equiv\hbar/J$ with J being the superexchange interaction (~ 0.1 eV).[24] In this case the hole carriers at the Fermi level may move coherently much longer than the observed spin-correlation length, when the traveling time of a hole carrier at the Fermi level over an area of the spin-correlation length which is given by $\tau_F\equiv\lambda_s/v_F$ is longer than τ_s, where v_F is the Fermi velocity of a hole carrier at the Fermi level. This is the case for underdoped LSCO, because τ_s is of the order of 10^{-14} sec while τ_F is of the order of 10^{-13} sec for the underdoped region of $x=0.10$–0.15 in LSCO. In this way the region of a metallic state becomes much wider than the spin-correlation length so as to reduce the increase of the kinetic energy due to the confinement of hole carriers in the spin-correlated region.

In this context Kamimura and Ushio treated the fourth term in Eq. (1), the exchange interaction between the spins of a dopant hole and a localized hole spin, in the mean-field approximation by replacing $\boldsymbol{S}_i$ by its average value $\langle\boldsymbol{S}\rangle$. Thus the effect of the localized hole spin system is dealt with as an effective magnetic field acting on the hole carrier. As a result they could separate the localized hole spin system in the AF order and the hole-carrier system and calculated the one-electron-type energy band for a carrier system assuming a periodic AF order.[25]

Thus, in the presence of the local AF ordering due to the localized hole spins in the CuO_2 layer, the hole carriers can move relatively freely in the CuO_2 plane by taking the characters of a Zhang-Rice spin-singlet state and a Hund's-coupling spin-triplet state alternately between neighboring sites. By averaging the character of wave function for each wave vector $\boldsymbol{k}$ over the Fermi surface for $x=0.1$ in LSCO, we have obtained the mixing ratio of characters of the Hund's coupling triplet state to the Zhang-Rice singlet state in the metallic state at the Fermi level, which is found to be 1 to 5. Thus the existence ratio of the Hund's coupling triplet state in the metallic state at the Fermi level is only 20%. This

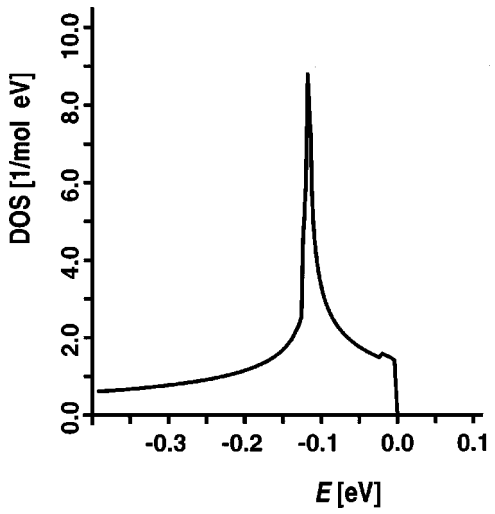

FIG. 2. The calculated density of states of LSCO based on the KS model as a function of energy. The energy is measured from the top of the conduction band calculated. A sharp peak at the energy around -0.1 eV corresponds to a saddle-point-type singularity at $(\pi/a,0,0)$ in the Brillouin zone.

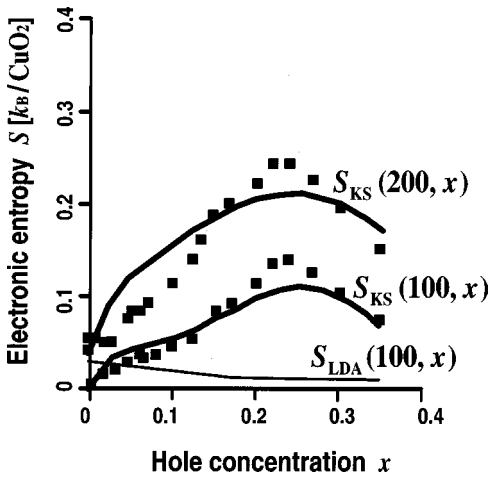

FIG. 3. The calculated electronic entropies of LSCO at $T=100$ K and $T=200$ K, $S_{\mathrm{KS}}(100,x)$, $S_{\mathrm{KS}}(200,x)$, based on the KS model (solid curves) and that of the "LDA state" at $T=100$ K, $S_{\mathrm{LDA}}(100,x)$, based on the LDA density of states (thin solid line). The experimental results of Loram *et al.* (Ref. 10) are also shown by solid squares for comparison. Note that both the calculated values and the experimental data for the 200 K entropy have been shifted to aid clarity.

value is close to the observed intensity ratio of the $\boldsymbol{E}\|c$ to the $\boldsymbol{E}\perp c$ polarization at the Cu L_3' satellite peak for $x=0.1$ in LSCO by Chen *et al.*[14]

The most important consequence of this treatment is that, having taken into account the strong spin exchange interactions in the mean-field approximation, the thermal and transport properties of the highly underdoped cuprates can be treated within a framework similar to a single-particle band structure. In this case, the assumption of an antiferromagnetic lattice is made, but the exchange interactions between dopant holes and this lattice obtained by their first-principles calculations are included in the single-particle band structure.

In 1997 Anisimov, Ezhov, and Rice calculated the energy band structure of the ordered alloy $La_2Li_{0.5}Cu_{0.5}O_4$ by the LDA+U method,[26] and they showed that a fairly modest reduction of the apical Cu-O band length is sufficient to stabilize the Hund's coupling spin triplet state with dopant holes in both b_{1g} and a_{1g}^* orbitals. Their result is consistent with the KS model. It should be remarked here that the effective Hamiltonian of the KS model, Eq. (1), has been solved recently by another method. That is the exact diagonalization method.[27] According to Hamada *et al.*,[27] computational studies by the exact diagonalization method for a 2D square lattice with $4\times4=16$ sites clearly showed that a hole carrier takes the characters of the Hund's coupling triplet state and of the Zhang-Rice spin singlet state alternately without destructing the AF order, supporting the KS model.

III. ELECTRONIC ENTROPY

Based on the one-electron-type energy band calculated by Ushio and Kamimura,[25] we have first calculated the density of states of the conduction band in LSCO, $\rho_{\mathrm{KS}}(\varepsilon)$, based on the KS model. The calculated result of $\rho_{\mathrm{KS}}(\varepsilon)$ is shown in Fig. 2. It has a sharp peak at $\varepsilon_{\mathrm{F}}(x)$ corresponding to $x\sim0.3$ in $La_{2-x}Sr_xCuO_4$. The appearance of this sharp peak is due to a saddle point singularity at $G_1=(\pi/a,0,0)$ in the Brillouin zone, where a is the Cu-O-Cu distance in a CuO_2 plane. Then, using $\rho_{\mathrm{KS}}(\varepsilon)$, we can calculate the doping (x) and temperature (T) dependences of electronic entropy $S(T,x)$ from the following well-known formula:

$$S(T,x)=-k_{\mathrm{B}}\int_{-\infty}^{\infty}[f(\varepsilon,\mu)\ln f(\varepsilon,\mu)+\{1-f(\varepsilon,\mu)\}\times\ln\{1-f(\varepsilon,\mu)\}]\rho(\varepsilon)\ d\varepsilon, \tag{2}$$

where $\rho(\varepsilon)$ is the density of states and $f(\varepsilon,\mu)$ the Fermi distribution function.

The calculated electronic entropies in LSCO at $T=100$ K and 200 K, $S_{\mathrm{KS}}(100,x)$ and $S_{\mathrm{KS}}(200,x)$, respectively, are shown by solid curves in Fig. 3, where the electronic entropy measured by Loram *et al.*[10] is also shown by solid squares for comparison. We find that both the calculated doping and temperature dependences of the electronic entropy, $S_{\mathrm{KS}}(100,x)$ and $S_{\mathrm{KS}}(200,x)$, are in good agreement with experimental results. It should be noticed that there are no adjustable parameters in the present calculation.

On the other hand, we have also calculated the electronic entropy by using the density of states derived from the conduction band in the ordinary band theory with a LDA, which corresponds to antibonding B_{1g} symmetry. This band has the main character of a Cu $d_{x^2-y^2}$ orbital. Shima *et al.*[19] have calculated the density of states for the b_{1g}^* energy band in LSCO, $\rho_{\mathrm{LDA}}(\varepsilon)$. By using $\rho_{\mathrm{LDA}}(\varepsilon)$ for $\rho(\varepsilon)$ in Eq. (2), we have calculated the electronic entropy as a function of hole concentration. The calculated values of the entropy in the LDA at $T=100$ K, $S_{\mathrm{LDA}}(100,x)$, are shown by thin solid line in Fig. 3. We see that calculated entropy based on

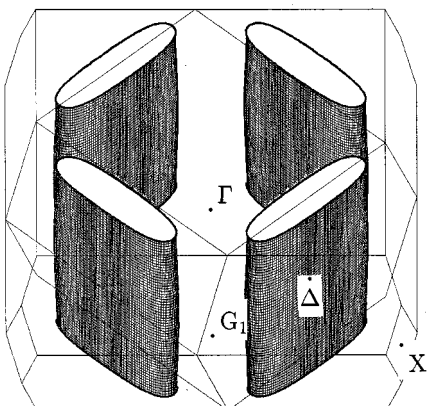

FIG. 4. The Fermi surface for $x=0.15$ based on the KS model. Here two kinds of Brillouin zones are also shown. One at the outermost part is the ordinary Brillouin zone and the inner part is the folded Brillouin zone for the antiferromagnetic unit cell in LSCO. Here the k_x axis is taken along $\overline{\Gamma G_1}$, corresponding to the x axis (the Cu-O-Cu direction) in real space, where $\Gamma=(0,0,0)$ and $G_1=(\pi/a,0,0)$.

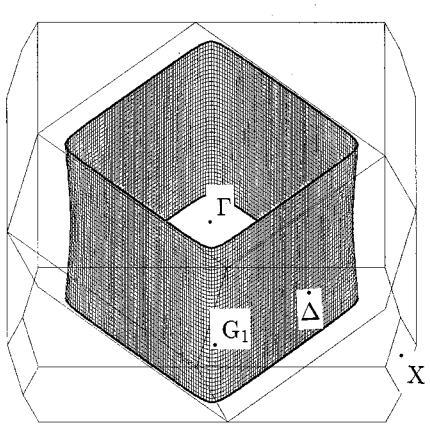

FIG. 5. The Fermi surface for $x=0.35$ based on the KS model. Here two kinds of Brillouin zones are also shown. One at the outermost part is the ordinary Brillouin zone and the inner part is the folded Brillouin zone for the antiferromagnetic unit cell in LSCO. Here the k_x axis is taken along $\overline{\Gamma G_1}$, corresponding to the x axis (the Cu-O-Cu direction) in real space.

$\rho_{\mathrm{LDA}}(\varepsilon)$ of the LDA band is too small, compared with experimental results. Thus we may say that the electronic structure based on the LDA band which we call ''LDA state'' may not be appropriate even for the overdoped region of cuprates. This means that both the local lattice distortion and strong correlation included in the KS model play important roles even in the overdoped region. From the present results, we suggest that the KS model may provide an appropriate description for the metallic state in cuprates.

IV. FERMI SURFACE

Based on the KS model, Ushio and Kamimura[25] calculated the Fermi surfaces for the underdoped regime of LSCO. We extend their calculations to the overdoped regime of LSCO. The Fermi surface structures calculated for $x=0.15$ and $x=0.35$ are shown in Fig. 4 and Fig. 5, respectively. Since only the dopant holes contribute to the Fermi surface, it consists of four small pockets in the underdoped regime for $x=0.15$. This unique feature of the Fermi surface structure is consistent with the experimental results of the angle-resolved photoemission spectroscopy (ARPES) for the superconducting $Bi_2Sr_{0.97}Pr_{0.03}CuO_{6+\delta}$ (Bi2201) compounds which includes a single CuO_2 layer in a unit cell, like LSCO.[28] Further the observed energy dispersion along the Γ-G_1 line for Bi2201 (Ref. 28) also coincides well with the one-electron-type energy band which includes the exchange interaction between the spins of a hole carrier and a localized hole.[25] Fermi surface structures for $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) determined by angle-resolved photoemission[29–31] are also very alike to the present result, although the Fermi surface structure for Bi2212 is more complicated due to the existence of two CuO_2 layers in a unit cell.

In particular, Aebi *et al.*[29] have found a $c(2\times2)$ superstructure on the Fermi surface suggesting the short-range antiferromagnetic correlation. It is easily seen that the ARPES results by Aebi *et al.* coincide well with the calculated Fermi surface in Fig. 4. This means that our prediction of a $\sqrt{2}\times\sqrt{2}$ antiferromagnetic local order has been proved experimentally. Further Marshall *et al.*[32] have also observed a small Fermi surface structure for the underdoped Dy concentration of $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$ with $T_c=65$ K, consistent with our prediction of a small Fermi surface.

The present calculation is based on a periodic system with the antiferromagnetic order. Since the region of the metallic state on the KS model is finite, as we described in Sec. II A, the appearance of the small Fermi surface structure should have a finite lifetime. As a result various phenomena based on the present small Fermi surface structure are also expected to have lifetime effects. For example, the observed outer edge of each pocket in the Fermi surface structure shown in Fig. 4 may not be sharp compared with its inner edge due to the above lifetime effect. This lifetime effect has recently been observed in the ARPES experiments, where the lifetime effect due to the vague outer edge of the Fermi surface has been called a ''shadow edge.''[30,31]

With the increase of doping, the Fermi surface changes from the structure of small pockets into a large Fermi surface, as is shown in Fig. 5 for $x\geqslant0.3$. Such a change of the Fermi surface from a small one to a larger one with increasing the hole concentration is also consistent with recent ARPES experimental results by Norman *et al.*[33] Wen and Lee also showed that small Fermi pockets at low doping continuously evolve into a large Fermi surface a high doping concentration.[34] Further, as regards the small pocket structure of Fermi surface, various theoretical groups have recently derived it theoretically.[35]

V. TRANSPORT PROPERTIES

A. Introduction

As other experimental evidence to support the KS model, we will discuss transport properties of cuprates, such as the resistivity and Hall effect in this section. In particular, we will show that the anomalous behaviors of the normal-state transport properties of cuprates can be explained by the KS model well.

B. Resistivity

We begin with discussing the anomalous behavior of resistivity of underdoped cuprates. The temperature dependence of the resistivity in the normal state of $La_{2-x}Sr_xCuO_4$ has been reported by Takagi *et al.*[36,37] In the underdoped region, it shows a linear temperature dependence in a wide temperature range from high temperatures above room temperature down to T_c. In this paper we will show that this anomalous linear temperature dependence in a wide temperature range down to T_c can be explained in terms of a small Fermi surface described in a previous section. For this purpose we have calculated the phonon-limited resistivity in LSCO from the variational expression for the resistivity of metals[38] by using the small Fermi surface in the KS model described in Sec. IV. The resistivity formula we have used is[38,39]

$$\rho(T)=\frac{A\pi}{2e^2k_BT}\int\int \omega_{\boldsymbol{q}}|g_{\boldsymbol{k},\boldsymbol{K}}|^2\left[\cosh\left(\frac{\hbar\omega_{\boldsymbol{q}}}{k_BT}\right)-1\right]^{-1}\times[(\boldsymbol{v}_{\boldsymbol{k}}-\boldsymbol{v}_{\boldsymbol{K}})\cdot\boldsymbol{u}]^2\frac{dS_{\boldsymbol{k}}}{v_{\boldsymbol{k}}}\frac{dS_{\boldsymbol{K}}}{v_{\boldsymbol{K}}}, \tag{3}$$

with

$$A=\left[\int\int(\boldsymbol{v}_{\boldsymbol{k}}\cdot\boldsymbol{u})(\boldsymbol{v}_{\boldsymbol{K}}\cdot\boldsymbol{u})(\boldsymbol{v}_{\boldsymbol{k}}\cdot\boldsymbol{v}_{\boldsymbol{K}})\frac{dS_{\boldsymbol{k}}}{v_{\boldsymbol{k}}}\frac{dS_{\boldsymbol{K}}}{v_{\boldsymbol{K}}}\right]^{-1}, \tag{4}$$

where $g_{\boldsymbol{k},\boldsymbol{K}}$ is the electron-phonon matrix element between the states of the wave vectors $\boldsymbol{k}$ and $\boldsymbol{K}$ of an electron which interacts with a phonon of the wave vector $\boldsymbol{q}$ and frequency $\omega_{\boldsymbol{q}}$ with $\boldsymbol{q}=\boldsymbol{K}-\boldsymbol{k}$, $\boldsymbol{v}_{\boldsymbol{k}}$ the group velocity of an electron in the state $\boldsymbol{k}$ which is given by $\boldsymbol{v}_{\boldsymbol{k}}=\partial E_{\boldsymbol{k}}/\partial\boldsymbol{k}$, $\hbar\omega_{\boldsymbol{q}}$ the phonon energy, $\boldsymbol{u}$ the unit vector in the direction of the external electric field which is parallel to the x axis, and $\int dS_{\boldsymbol{k}}$ an integration over the Fermi surface. Since the Fermi surface section in the k_x-k_y plane is small, the phonons of small wave vectors are involved in the mechanism of causing resistivity. Thus $g_{\boldsymbol{k},\boldsymbol{K}}$ is expressed by the following form: $|g_{\boldsymbol{k},\boldsymbol{K}}|^2=(N/2M\omega_{\boldsymbol{q}})(\boldsymbol{C}\cdot\boldsymbol{q})^2$, with $\boldsymbol{C}$ being a coupling constant whose dimension is energy. Further the phonon dispersion along the c axis is small, so that we have expressed the phonon dispersion in a two-dimensional $\boldsymbol{q}$ space as $\hbar\omega_{\boldsymbol{q}}=v_sq_\perp=v_s\sqrt{q_x^2+q_y^2}$, with the sound velocity v_s whose value is 5×10^5 cm/s for LSCO.[40] The calculated results of resistivity in the ab plane of LSCO are shown in Fig. 6 as a function of temperature T for $x=0.05$, 0.1, and 0.15 in $La_{2-x}Sr_xCuO_4$. Because the resistivity in the underdoped region of LSCO is governed by the electron-phonon scattering with small momentum transfer due to the small Fermi surface of LSCO, a linear temperature dependence of the resistivity appears in a wide temperature range, consistent with the observed resistivity in the normal state of $La_{2-x}Sr_xCuO_4$ by Takagi *et al.*[37] For values of x above 0.18, the observed temperature dependence in resistivity deviates upward from the linear dependence in a low-temperature region. Since this deviation is more remarkable for sintered samples,[36,37] such a deviation might be due to disordered effects.

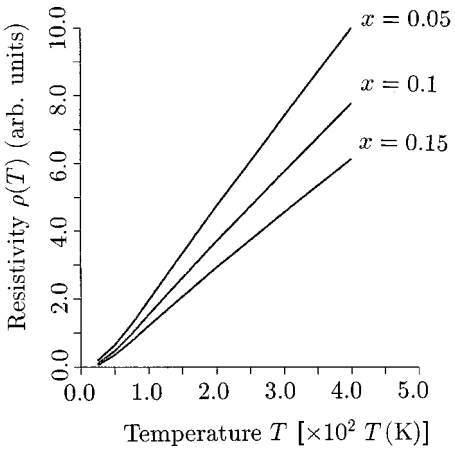

FIG. 6. The calculated temperature dependence of the resistivity in the ab plane of LSCO for various hole concentrations, based on the KS model.

C. Hall effect

The observed Hall coefficient of LSCO, R_H, has also shown an anomalous behavior. The Hall data in LSCO show a drop in R_H by two orders of magnitude as x increases from $x=0.1$ to 0.3. Then a sign change of R_H from a holelike to an electronlike character occurs at around $x=0.3$.[36,41,42] In this section we will show that these anomalous behaviors of the Hall coefficient can be explained by the KS model without introducing any adjustable parameters.

For this purpose we use the formula derived by Schimizu and Kamimura,[43] by substituting $-\partial f/\partial E_{\boldsymbol{k}}$ for the δ function in their formula. The formula for the Hall coefficient R_H thus obtained is given as follows:

$$R_H=\frac{4\pi^3}{ec}\frac{\int_{BZ}d\boldsymbol{k}\frac{\partial E_{\boldsymbol{k}}}{\partial k_x}\left[\frac{\partial E_{\boldsymbol{k}}}{\partial k_x}\frac{\partial^2E_{\boldsymbol{k}}}{\partial k_y^2}-\frac{\partial E_{\boldsymbol{k}}}{\partial k_y}\frac{\partial^2E_{\boldsymbol{k}}}{\partial k_x\partial k_y}\right]\left(-\frac{\partial f}{\partial E_{\boldsymbol{k}}}\right)}{\left[\int_{BZ}d\boldsymbol{k}\left(\frac{\partial E_{\boldsymbol{k}}}{\partial k_x}\right)^2\left(-\frac{\partial f}{\partial E_{\boldsymbol{k}}}\right)\right]^2}, \tag{5}$$

where $E_{\boldsymbol{k}}$ represents the energy dispersion of a conducting hole. By using the effective one-electron-type energy band for the hole carriers derived by Ushio and Kamimura for LSCO,[25] we have calculated both the hole-concentration and temperature dependences of R_H. The calculated results of R_H in $La_{2-x}Sr_xCuO_4$ for $T=80$ K and 300 K are given as a function of x in Fig. 7, where the experimental results of R_H by Takagi *et al.*[36] are also shown for comparison. It is seen from this figure that the calculated results of R_H decreases

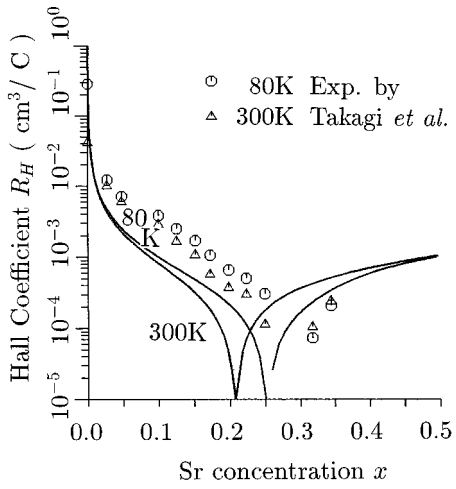

FIG. 7. The calculated concentration dependence of the Hall coefficient R_{H} for $T=80$ K and $T=300$ K based on the KS model, together with the experimental results by Takagi *et al.* (Ref. 36).

like $1/x$ in very low concentrations. Then in the underdoped to overdoped region it decreases more rapidly than the $1/x$ behavior and at around $x\sim 0.3$ the Hall coefficient changes its sign from positive (hole like) to a negative one (electron like). This behavior in the x dependence of R_{H} coincides well with the experimental results by Takagi *et al.*[36] According to the present theoretical result, the reason for the sign change of R_{H} is due to the fact that, in the region of $0.3\geqslant x$, the four small pockets of the Fermi surface change into a large Fermi surface and that, on the large Fermi surface, the second derivatives of the energy dispersion such as $\partial^2 E_{\boldsymbol{k}}/\partial k_y^2$ change sign over a dominant region of the Fermi surface. This leads to the negative Hall coefficient R_{H} at $T=0$ K in this concentration region. When temperature increases, the holes with higher energy than the Fermi energy contribute more to the Hall coefficient of a negative sign. In other words, at a higher temperature than 300 K the dominant number of holes lie on the states for which the second derivatives of the energy dispersion is negative. As a result the Hall coefficient becomes negative at higher temperatures. In this way the KS model can explain the anomalous behavior of the observed Hall effect without introducing any disposal parameter.

VI. CONCLUSION

In order to clarify the feature of a metallic state in superconducting cuprates, we have first calculated the electronic entropy of LSCO using the two kinds of density of states derived from first-principles calculations, the one from the KS model and the other from the LDA band structure. It was shown that the observed peculiar doping dependence and the absolute magnitudes of electronic entropy reported by Loram *et al.*[10] can be explained by the KS model without any adjustable parameters. In contrast, an LDA band structure gives entropy values which are too small even in the overdoped region. We have further shown that the temperature and hole-concentration dependences of the resistivity and of the Hall effect calculated on the basis of the KS model can explain well the characteristic features of observed anomalous transport properties. From these results, we would like to suggest that the Kamimura-Suwa model may provide an appropriate description for the metallic state in cuprates, while the ''LDA state'' may not be appropriate even for the highly overdoped region of cuprates.

ACKNOWLEDGMENTS

It is a great pleasure to acknowledge stimulating conversations and valuable discussions with Professor W. Y. Liang from University of Cambridge, who stayed in Science University of Tokyo as a visiting professor in the 2000 academic year. The numerical calculations were performed at the Information Technology Center, the University of Tokyo.

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