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Hall coefficients and optical properties of $La_{2-x}Sr_xCuO_4$ single-crystal thin films

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The low-field Hall coefficient R_H, optical reflectance and transmittance of the $La_{2-x}Sr_xCuO_4$ system with various Sr concentrations from $x=0$ to 0.36 are systematically studied using single-crystal thin films epitaxially grown on (100) face $SrTiO_3$ substrates with the c axis normal to the film surface. For the x range measured, R_H is positive and decreases more rapidly than that expected from the Sr concentration but more slowly than reported earlier for polycrystalline specimens, indicating anisotropy of R_H. Furthermore, the x dependence indicates deviation from that expected from a simple band model. Within the superconducting composition range, R_H exhibits characteristic temperature dependence. The optical reflectance spectrum changes from that of a semiconductor at $x=0$ to a typical metallic one characterized by the Drude model for $x>0.1$, indicating the development of itinerant holes in the Cu-O planes. In the optical transmission spectra, an anomalous absorption band is seen in addition to the fundamental absorption corresponding to an energy gap of about 2 eV. This band, which develops with Sr doping, implies an enhancement of the density of states near the Fermi level. Taking these observations into account, the normal-state transport properties are explained with a qualitative consistence.

I. INTRODUCTION

Since high-T_c superconductivity was discovered by Bednorz and Müller,[1] enormous effort has been devoted to this field, giving rise to a series of discoveries of superconducting cuprate materials.[2-6] Extensive progress has been made toward the understanding of high-T_c superconductivity. Most importantly, isotope-effect measurements by Batlogg and co-workers[7,8] showed a very small isotope shift in $La_{2-x}Sr_xCuO_4$ and $Ba_2YCu_3O_{7-y}$. The absence of resistivity saturation at high temperatures in both materials observed by Gurvitch and Fiory[9] indicated extremely small electron-phonon interaction. These results suggested that the high-T_c superconductivity may be mediated by electronic interaction rather than phonons. On the other hand, inelastic neutron scattering measurements by Shirane *et al.*[10,11] indicated that the magnetic interaction seems to play an important role in this superconductivity. However, in spite of the extensive theoretical[12,13] and experimental studies covering the various approaches to the clarification of high-T_c superconductivity, much research remains.

For understanding high-T_c superconductivity of cuprate materials it is widely accepted that the $La_{2-x}Sr_xCuO_4$ system is the prototype, and that it is of primary importance to clarify the normal-state physical properties of this system. The most important clue is that Sr doping changes this material systematically from an antiferromagnetic insulator to a superconducting metal with $T_c \approx 40$ K. (This behavior is analogous to the $Ba_2YCu_3O_{7-y}$ system, where the electronic properties change quite similarly to the La-Sr-Cu-O system by the incorporation of oxygen.) Therefore, Sr doping and the observation of systematic change in the normal-state properties due to this doping provide valuable insight into the nature of high-T_c superconductivity in this system.

This paper reports an experimental study on the transport and optical properties of the La-Sr-Cu-O system as a function of Sr concentration x for single-crystal thin films epitaxially grown on (100) $SrTiO_3$ substrates. Thus far, the normal-state transport properties of the La-Sr-Cu-O system have been measured in most cases on sintered polycrystalline specimens and only a few experiments have been made on single crystals. Since the properties of the La-Sr-Cu-O system are strongly anisotropic, measurement of the transport and optical properties using single crystals is of great importance. On the other hand, there are large discrepancies in the electronic density of states in this system between band calculations and experiments, e.g., x-ray photoemission spectroscopy,[14] and electron-energy-loss spectroscopy.[15] The optical absorption spectrum also provides information on the electronic density of states, although there have been no reports on it. We used thin films to measure optical transmittance, by which the band structure of this system can be inferred to some extent.

In this research, several characteristic features have been revealed. Normal-state properties change systematically with Sr doping, generally in agreement with the earlier work by Ong *et al.*[16] and Uchida *et al.*[17] In the Hall coefficient R_H, we find a characteristic temperature dependence, which is confined to the superconducting composition range. Since the present system can be viewed as one where two-dimensional (2D) spin fluctuation is strong, the possibility of skew scattering is also examined, which arises from the local moments associated with Cu^{2+} states.

In the x dependence of R_H, we observed a much faster decrease in R_H than expected from the Sr concentration in the composition range of $x>0.1$, when it is assumed that the Sr incorporation provides one hole per atom. This tendency is interpreted as the coexistence of two types of carriers associated with the band structure.

In the optical transmission spectra of La_2CuO_4 films we find an absorption edge corresponding to a band gap of about 2 eV. This edge splits due to Sr doping. As Sr is doped, the lower edge shifts toward lower energies to form an absorption peak, indicating a dramatic change in the band structure. This absorption is considered to reflect the modified density of states near the top of the lower filled band caused by the incorporation of Sr. This change in the band structure is discussed in relation to the rapid decrease in R_H with x.

In the reflection spectra of La-Sr-Cu-O epitaxial films, which generally follow the Drude model, we find another oscillating peak centered at 1.8 eV. This corresponds to the enhanced density of states near the top of the valence band and is in agreement with the results of the optical transmission experiments.

When taking into account the correlation of the present absorption spectra with the superconductivity, the existence of spin fluctuation and the enhanced density of states at the top of the valence band have close relevance to the occurrence of the superconductivity in the copper-oxide based superconductors.

II. EXPERIMENTAL PROCEDURES

A. Sample preparation

Samples used were La-Sr-Cu-O epitaxial thin films grown on $SrTiO_3$ (100) substrates by the rf magnetron sputtering method.[18] The c axis of the La-Sr-Cu-O is normal to the film surface. The substrate temperature for epitaxial growth was 800 °C. Sputtering targets were compounds of various [Sr]/[La] ratio ($x=0$, 0.04, 0.1, 0.15, 0.2, 0.24, 0.3, 0.4) with 20% excess CuO. After repeated trials target compositions were optimized so that the film stoichiometry could be attained.

Film compositions were determined by x-ray fluorescent analysis and Rutherford backscattering. It was confirmed that the film compositions are homogeneous along the thickness direction and the [Sr]/[La] ratios were the same or slightly less (less than 10%) than those of the targets except for $x=0.4$. For the films prepared from the target having the [Sr]/[La] ratio of 0.2, x became 0.36 ± 0.02 when epitaxial growth was attained. It is known that in bulk La-Sr-Cu-O materials a single phase can be attained when $x<0.4$ (Ref. 19). In the present study, single-phase films with $x\approx0.4$ were obtained only nonepitaxially. The large discrepancy of x between films and the target in the case of $x=0.4$ can be ascribed to the difficulty in increasing the doping amount more than 0.3. Figure 1 shows a typical x-ray diffraction pattern for one of the epitaxial films, indicating that the film grows epitaxially with the c axis normal to the film surface. Reflection high-energy electron diffraction (RHEED) patterns for these films show streaky patterns and in several films Kikuchi bands, indicating that the films are single crystalline with a very smooth surface. Channeling spectroscopy measurement was also carried out for several films.[20] When the incident α-particle beam of 7 MeV was normal to the film, backscattering yield decreased to $\frac{1}{4}-\frac{1}{3}$, indicating again epitaxial growth.

Although the as-deposited films were superconducting, they were annealed at 800 °C for 8 h in air after deposition in order to minimize remaining oxygen vacancies. Through this annealing process, T_c was improved by a few degrees but resistivity ρ remained almost unchanged. Also, surface roughness increased due to annealing but it was still below 100 Å.

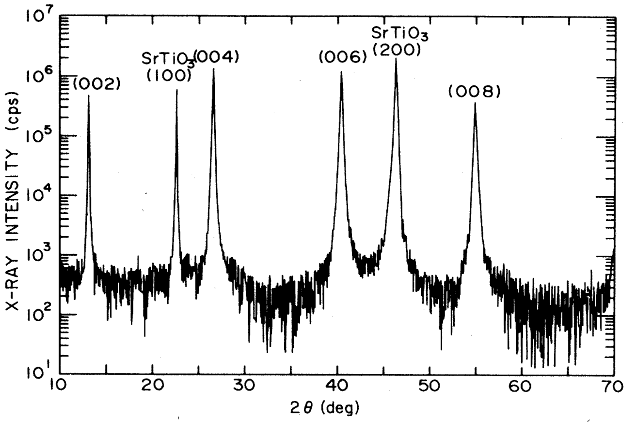

FIG. 1. X-ray (Cu $K\alpha$) diffraction pattern for a La-Sr-Cu-O ($x=0.15$) thin film, showing epitaxial growth of the La-Sr-Cu-O (001) plane.

Film thickness, measured with a stylus profilometer, ranged from 3000 to 4000 Å. The films were patterned into a rectangular shape (4.6×0.8 mm^2) with eight terminals for the measurements of ρ and R_H. Electrodes were formed with evaporated Au films and silver paste, followed by heat treatment at 400 °C for 30 min in air. The lattice constants of the films were known only for the c axis. They varied from 13.2 to 13.3 Å with a tendency to increase with an increase in x.

B. Transport and optical measurements

Hall coefficient was measured under a magnetic field H of 7700 Oe in the temperature range from the point above T_c to 300 K. The Hall coefficient measured is considered to be within the low-field Hall effect regime, where electron scattering plays a dominant role. Current density for the Hall measurement was set from 10 to 10^3 A/cm^2, depending on the resistance of the samples. The temperature dependence of ρ for determining the resistive superconducting transition temperature was measured separately with the current density below 5 A/cm^2. The results for both measurements were the same, indicating slight influence of Joule heating. The temperature was determined with a germanium thermometer and an alumel-chromel thermocouple in the absence of a field.

Optical transmission and reflection spectra were measured with a monochromator in the wavelength range from 0.4 to 4.5 μm at room temperature. The reflectance was calibrated with a silver thin film. Most of the samples for optical measurement were annealed in air. For several films, the reflectance and transmittance spectra were measured before and after annealing, but no appreciable change was recognized except for the films with $x\leq0.04$.

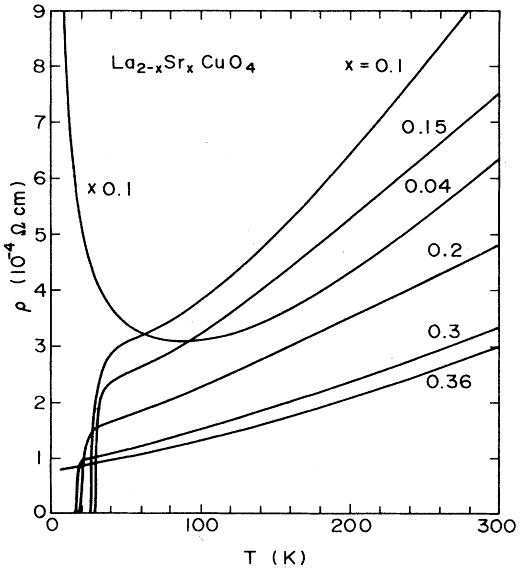

FIG. 2. Temperature dependence of resistivity ρ within the Cu-O planes for the La-Sr-Cu-O (001) epitaxial thin films with x from 0.04 to 0.36.

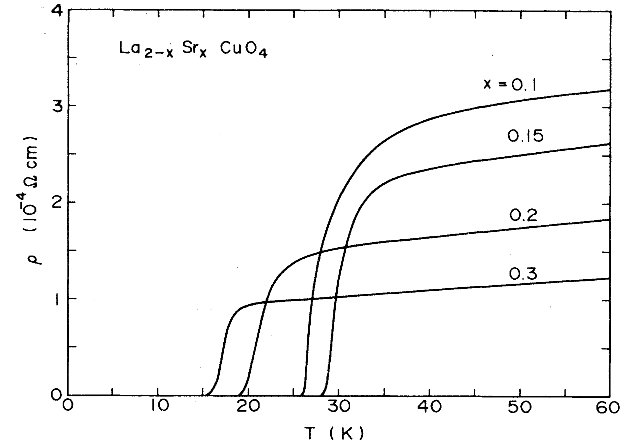

FIG. 3. Resistive superconducting transitions for the La-Sr-Cu-O epitaxial films with $x=0.1$, 0.15, 0.2, and 0.3.

III. TRANSPORT PROPERTIES

A. Resistivity and T_c

The temperature dependence of ρ is shown in Fig. 2 for the series of La-Sr-Cu-O epitaxial films with x ranging from 0.04 to 0.36. Superconductivity was observed for the films with $0.1 \leq x \leq 0.3$. The temperature dependence of ρ showed metallic behavior for all the films except for $x=0.04$ below 150 K. For $x=0.1$, no upturn was observed in the $\rho - T$ curve above T_c, which was observed in bulk polycrystals.[19,21] This indicates that the amount of oxygen vacancies was considerably reduced in our epitaxial films. With the increase in x, ρ decreased systematically, generally in agreement with the earlier work on sintered polycrystals by Tarascon *et al.*,[19] except for absolute values. Another different behavior is the T dependence of ρ, which deviates appreciably from the linear dependence as observed in bulk polycrystalline La-Sr-Cu-O and $Ba_2YCu_3O_{7-y}$ specimens.[9,19,21] In our epitaxial films $d\rho/dT$ decreases significantly at lower T.

Figure 3 shows the resistive superconducting transition for $x=0.1$, 0.15. 0.2, and 0.3. $T_c(R=0)$ is the highest for $x=0.15$ as in the case of sintered materials. The superconducting transition width ΔT_c defined by twice the width between the midpoint and the zero-resistance point is 2.7 K for $x=0.15$ and increased to greater than 4 K for $x>0.2$. Table I summarizes the data for T_c, ΔT_c, ρ, and $d\rho/dT$. The lower T_c and broader resistive transition were also observed in bulk single crystals.[22] These characteristics seem to be intrinsic to single crystalline La-Sr-Cu-O, where inhomogeneity of Sr distribution always exists to a certain extent due to the essential nature characteristic of a solid solution. This is in contrast to the case of Ba-Y-Cu-O which has well-defined stoichiometry.

The temperature dependence of ρ for $x=0.04$ shows incipient localization behavior below 150 K. Figure 4 shows the linear relationship between $\ln\rho(T)$ and $T^{-1/3}$ for three samples with $x=0.04$, indicating that electronic conduction below 150 K is most likely due to the variable range hopping in the 2D system. From this the electronic conduction in the La-Sr-Cu-O system is essentially 2D. It is also supposed that at $x=0.04$ the Fermi level is very close to the band edge of the extended states and that there is a noticeable amount of localized states in this system with low Sr concentration. For films with $x=0$, $\rho(T)$ behaved like a semiconductor with 2D variable-range-hopping conduction in the entire temperature range measured, as previously reported by Oda *et al.*[23]

TABLE I. Properties of $La_{2-x}Sr_xCuO_4$ (001) epitaxial thin film specimens. ρ is in-plane resistivity. ΔT_c is defined in the text.

x	ρ(40 K) (10^{-4} Ω cm)	ρ(300 K) (10^{-4} Ω cm)	$d\rho/dT$(300 K) (μΩ cm/K)	T_c (K)	ΔT_c (K)
0	7.8×10^4	3.46×10^3	...	...	...
0.04	37.0	63.1	52	...	...
0.1	2.87	9.58	3.2	26.2	2.9
0.15	2.36	7.5	2.3	28.6	2.7
0.2	1.65	5.31	1.5	18.9	4.5
0.3	1.09	3.33	1.0	15.2	4.1
0.36	0.96	2.99	0.96	...	...

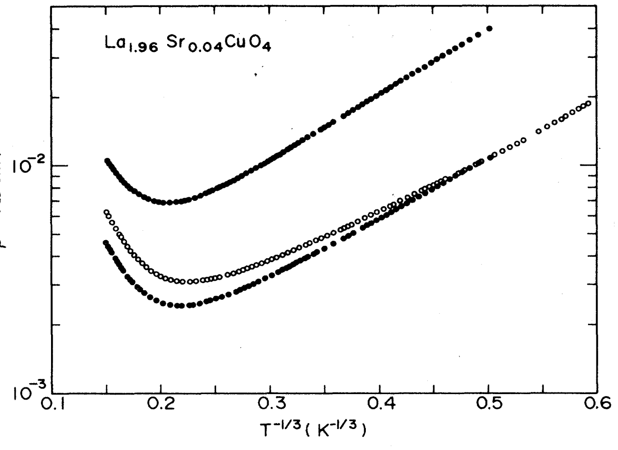

FIG. 4. In ρ vs $T^{-1/3}$ for the La-Sr-Cu-O epitaxial films with $x = 0.04$. Open circles indicate the same sample in Fig. 2.

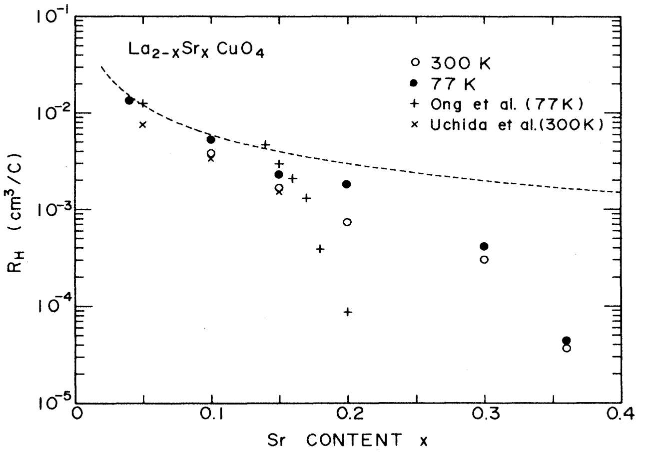

FIG. 5. Composition dependence of Hall coefficient R_H for the La-Sr-Cu-O epitaxial films at 77 and 300 K. Magnetic field is parallel to the c axis and the current is along the Cu-O plane. + and × denote the data for sintered polycrystalline specimens by Ong *et al.* (Ref. 16) at 77 K and by Uchida *et al.* (Ref. 17) at 300 K, respectively. The broken line indicates the Sr concentration x in the form of $V_0/2c$ (see text).

B. Hall coefficient R_H

Figure 5 shows R_H at 77 and 300 K for the La-Sr-Cu-O epitaxial films as a function of Sr concentration x, together with the data for sintered specimens reported by Ong *et al.*[16] and Uchida *et al.*[17] The broken line indicates $R_H = V_0/2ex$, where $V_0 = 190$ Å^3 is the unit-cell volume, when it is assumed that the substituted Sr ions supply one hole per atom. The Hall carrier density n_H defined as $n_H = 1/eR_H$ coincides with the Sr concentration in the range of $x \leq 0.1$, as clearly shown in Fig. 4. As x exceeds 0.1, R_H begins to deviate from the $V_0/2ex$ curve noticeably. This behavior with increasing x was observed earlier by Ong *et al.*[16] in their Hall measurements on polycrystalline La-Sr-Cu-O specimens. The significant difference between the epitaxial films and the polycrystalline specimens can be observed when $x > 0.15$ and the difference increases with increasing x. This difference in R_H can be ascribed to the anisotropic Hall effect, which was expected both theoretically[24,25] and experimentally.[26] When the magnetic field H is applied parallel to the basal plane, R_H becomes very small. In addition, taking into account the fact that the difference increases with increasing x, it is also likely that the anisotropy ratio increases with increasing x. This tendency was also predicted by Allen, Pickett, and Krakauer[24,25] in the theoretical calculation of the transport properties based on their band calculation results. According to them, the anisotropy ratio increases with x toward $x = 0.24$, where R_H for the Cu-O planes vanishes.

In these experiments, the positive R_H persists up to $x = 0.36$ and the sign reversal of R_H near $x = 0.24$ was not observed. However, in our polycrystalline La-Sr-Cu-O films where the c axis is partially normal to the film surface and partially parallel to the film with $x \approx 0.4$, negative R_H was observed and is in agreement with the above.

The temperature dependence of R_H for x from 0.04 to 0.36 is shown in Figs. 6(a)–6(f). For $x = 0.04$, R_H is nearly constant over the temperature range measured. Carrier density for this composition derived from R_H is 4.8×10^{20} cm^{-3}, which nearly coincides with the Sr concentration. For $x = 0.36$, where superconductivity is not observed above 4.2 K, R_H is pronouncedly reduced and exhibits complex behavior compared with other compositions. With falling temperature, R_H decreases to 2.5×10^{-5} cm^3/C at 150 K, then abruptly increases to the highest value of 7.3×10^{-5} cm^3/C at 20 K. For the superconducting compositions ($0.1 \leq x \leq 0.3$), R_H has a rather common T dependence, which seems to be characteristic of superconducting compositions. In this range of x, R_H increases with decreasing temperature to its maximum point at a temperature of $T_1 \approx 10$–80 K. This behavior is persistent among superconductivity compositions and seems to be closely related to the high-T_c superconductivity in cuprate materials. The T dependence of R_H is generally similar to that of the Ba-Y-Cu-O system, and this behavior seems to be common to the Cu-O–based superconductors.[27]

Figures 6 also shows the temperature dependence of Hall carrier density n_H. For $T > T_1$, n_H is almost linear in T. This linear T dependence is also observed in single crystals[28] and polycrystals of Ba-Y-Cu-O,[29] where n_H is not only linear but $n_H \propto 1/T$. However in the present experiment, n_H behaves as $n_H = a + b/T$, except for the region near and below T_1.

Since the samples in Figs. 6 are all metallic, it is quite unlikely that the carrier density decreases with decreasing T and increases below T_1. Therefore, it should be taken into account that the T dependence of R_H reflects the effects other than carrier localization. This is discussed next.

In metals with magnetic impurities, R_H usually shows significant temperature and magnetic field dependence, known as skew scattering.[30] In the present La-Sr-Cu-O system, there is a possibility that Cu^{2+} ions may behave as localized magnetic moments, and at first sight it is natural to associate the observed temperature dependence of

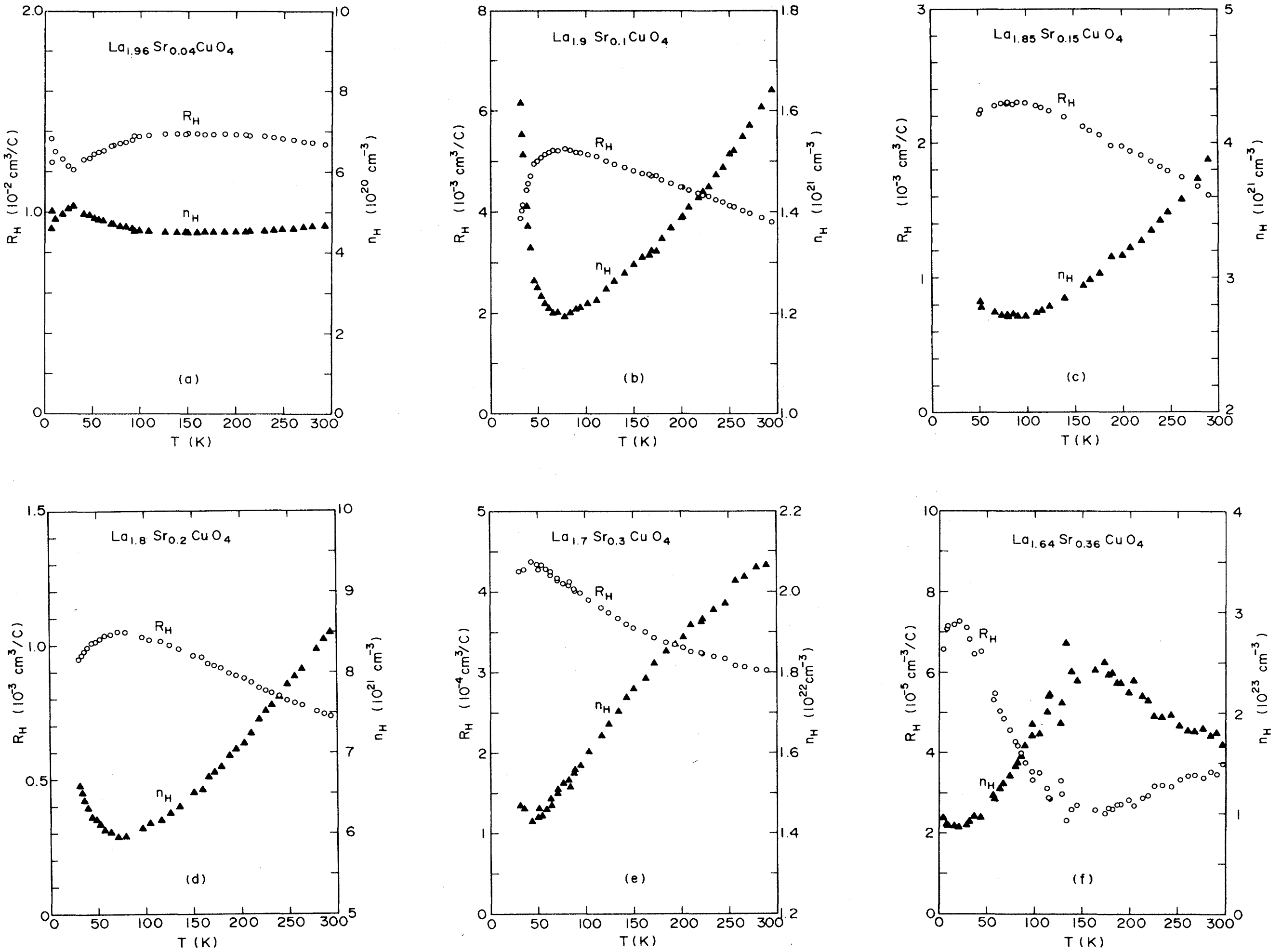

FIG. 6. Temperature dependence of Hall coefficient R_H and Hall carrier density n_H for the La-Sr-Cu-O epitaxial films. (a) $x=0.04$, (b) $x=0.1$, (c) $x=0.15$, (d) $x=0.2$, (e) $x=0.3$, and (f) $x=0.36$.

R_H with skew scattering. Then we measured the magnetic field dependence of R_H for the $x=0.15$ film up to 12 T at three temperatures, the results of which are shown in Fig. 7. Hall resistance R_{xy}, the Hall voltage divided by the injecting current, showed good linear H dependence at the three temperatures (i.e., below, near, and above T_1), and no sign of nonlinearity was observed. This indicates that there is probably no effect from skew scattering at least for carriers within the Cu-O planes.

These results do not necessarily mean that there is no local magnetic moment in the La-Sr-Cu-O system. Because skew scattering arises through spin-orbit interaction between conduction carriers and localized moments, the present results might imply that the spin-orbit interaction is very weak in this system.

Figure 8 shows Hall mobility μ_H for the La-Sr-Cu-O epitaxial films. Except for $x=0.04$, μ_H increases with the decrease in temperature, indicating dominant scattering by phonons. This behavior is in contrast to the $\mu_H(T)$ observed for $BaPb_{1-x}Bi_xO_3$, where doping with Bi is made

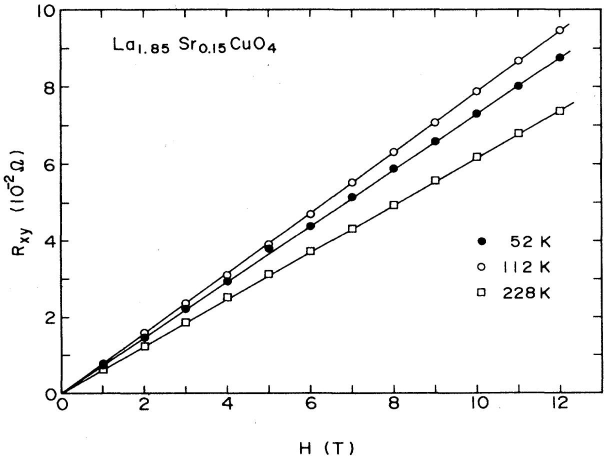

FIG. 7. Magnetic field dependence of Hall resistance R_{xy} for a $La_{1.85}Sr_{0.15}CuO_4$ epitaxial film at three temperatures.

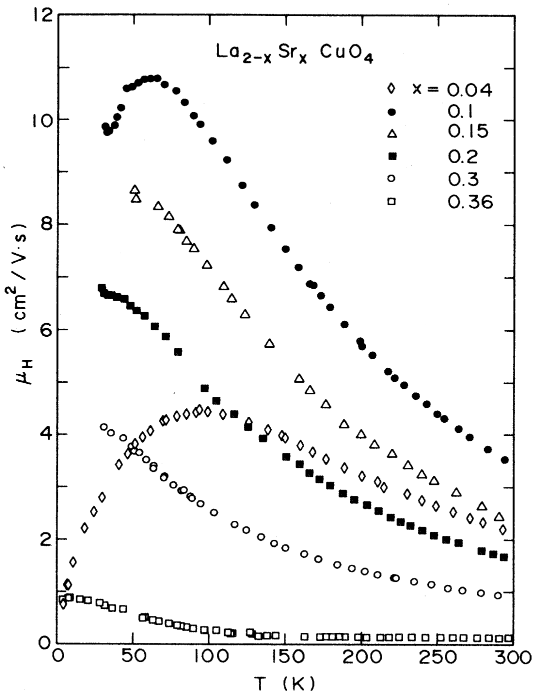

FIG. 8. Temperature dependence of Hall mobility μ_H for the La-Sr-Cu-O epitaxial films with x from 0.04 to 0.36.

into oxygen octahedral sites and impurity scattering plays a dominant role.[31] For $x=0.04$, μ_H decreases due to localization. The decrease in μ_H with x is due to the apparent decrease in R_H as shown in Fig. 5.

IV. OPTICAL PROPERTIES

A. Reflectance

Figure 9 shows the reflectance (R) spectra for the La-Sr-Cu-O epitaxial films in the wavelength (λ) range from 0.4 to 4.5 μm. For the semiconducting composition $x=0$, no sign of plasma reflection was observed for $\lambda < 4.5$ μm. For $x=0.04$, where ρ behaves like a metal at high temperatures, an increase in R for $\lambda > 1.7$ μm was observed, presumably indicating plasma reflection. As x increases from 0.04, the plasma reflection becomes clearer and R increases to about 75% at 4.5 μm with the plasma edge at $\lambda \approx 1.5$ μm, which changes only slightly with x. In addition to the plasma edge, there are small structures in the shorter than 1.5 μm wavelength range. The peak centered at $\lambda=0.8$ μm shifts toward shorter λ with x and disappears at $x=0.1$, while the peak centered at $\lambda=1.4$ μm also shifts to the shorter wavelength and persists up to $x=0.36$. These structures in R were also observed for polycrystalline specimens,[32-36] although the origins were not assigned clearly. Since the reflection spectrum of a solid in the short λ range generally reflects electronic band structure, it seems reasonable that these peaks are related to some structures in the joint density of states (JDOS) corresponding to the energy of 1.6 and 0.9 eV, respectively.

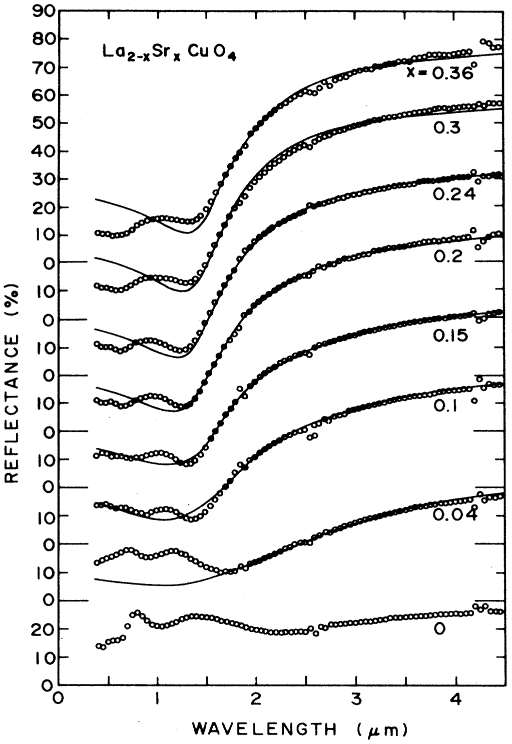

FIG. 9. Reflectance spectra for the La-Sr-Cu-O (001) epitaxial films with x from 0 to 0.36. Electric field is parallel to the Cu-O plane. The scales are shifted by an appropriate value. Solid lines are Drude fits. The fitting parameters ω_p and $\tau(=1/\gamma)$ are shown in Fig. 10. ϵ_∞'s are 3.2, 5.1, 5.1, 5.6, 6.1, 8, and 8.5 for x from 0.04 to 0.36 in order of increasing x.

The solid curves in Fig. 9 are the best fits to the Drude model using the following equation

$$\epsilon(\omega)=\epsilon_\infty\left[1-\frac{\omega_p^2}{\omega^2+i\omega\gamma}\right],$$

where ϵ_∞ is the optical dielectric constant, ω_p the plasma frequency, and $\gamma=1/\tau$ the damping factor or the electron scattering rate. The fits in the longer than 1.5 μm λ range are quite good, especially for samples with $x=0.15$ and 0.2, while they are poor in the shorter than 1.5 μm λ range because of the structure. The systematic change in $R(\omega)$ with increasing x reflects the change in the electronic structure of the La-Sr-Cu-O system by Sr doping. It also indicates that the La-Sr-Cu-O system becomes more metallic even in the x range where superconductivity disappears. Figure 10 shows the systematic change of ω_p and τ with x. As x increases, τ increases from 5.2×10^{-15} s at $x=0.04$ to 1.3×10^{-14} s at $x=0.3$. This implies that the Fermi level E_F in the La-Sr-Cu-O system shifts from the point near the band edge where the localized states probably due to oxygen vacancies dominate electron scattering to the point well below the band edge. On the other hand, ω_p gradually decreases when x exceeds 0.2. This behavior was observed by Tajima *et al.*[32] and interpreted by the half-filled band based on the 2D tight-binding models, although it is inconsistent to the observed Hall coefficients.

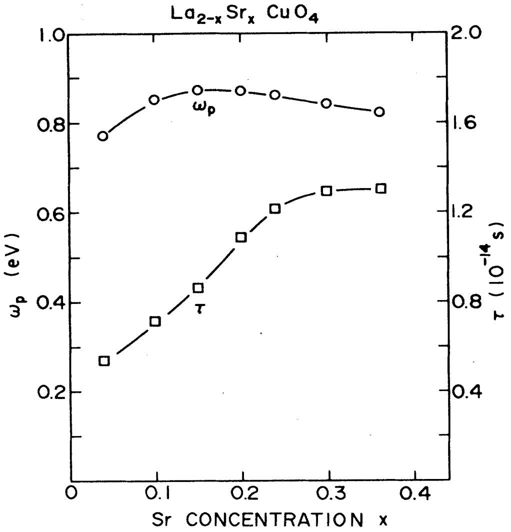

FIG. 10. Sr concentration x dependence of ω_p and $\tau(=1/\gamma)$ derived from the Drude fitting for the data in Fig. 9.

The value of $\omega_p = 0.87$ eV is nearly the same as the one obtained by Orenstein *et al.*[34] and Tajima *et al.*[32] for the polycrystalline specimens.

Using the relation $\omega_p^2 = 4\pi ne^2/\epsilon_\infty m^*$, it is possible to estimate the optical effective mass m^* of the La-Sr-Cu-O system. If the value for n derived from R_H is used, the effective-mass ratio m^*/m_0 becomes 0.9 and 3.4 for $x=0.15$ and 0.2, respectively. Since n_H is significantly larger than the carrier density especially for $x \gtrsim 0.15$, m^*/m may become much smaller. This indicates that the carriers are not likely $3d$ holes on Cu atoms, as suggested by Fujimori and co-workers[14,37] in their x-ray photoemission spectroscopy and by Nücker *et al.*[15] in their electron-energy-loss spectroscopy (EELS).

B. Optical absorption

Figure 11 shows the optical transmittance $T(\lambda)$ in the λ range from 0.4 to 4.5 μm for the La-Sr-Cu-O (001) epitaxial films. For $x=0$, the rise in $T(\lambda)$ at $\lambda = 0.5$ μm and the large transmittance for $\lambda > 0.6$ μm indicates the existence of the band gap of about 2 eV in the undoped La_2CuO_4. When Sr ions are doped, the transmittance in the infrared decreases dramatically, indicating free-carrier absorption. On the other hand, the rise in $T(\lambda)$ shifts to shorter λ with x, and this rise in transmission substantially disappears for $x > 0.3$, at least in the longer than 0.4-μm λ range.

Because the transmission spectra were measured on the epitaxial thin films deposited on $SrTiO_3$ substrates, the effects of interference should be taken into account. However, the absorption coefficient α of 5×10^4 cm^{-1} at 1 μm for $x=0.1$ and a film thickness of no less than 3000 Å rule out the effect of interference in the spectra for $x > 0.1$. Even for $x=0$ and $x=0.04$ it is clear from Fig. 11 that the effect of interference is very weak. Therefore, the structure for $\lambda < 1.5$ μm presumably reflects the band structure in the La-Sr-Cu-O system, which is quite sensitive to the Sr doping, and hence the electronic structure.

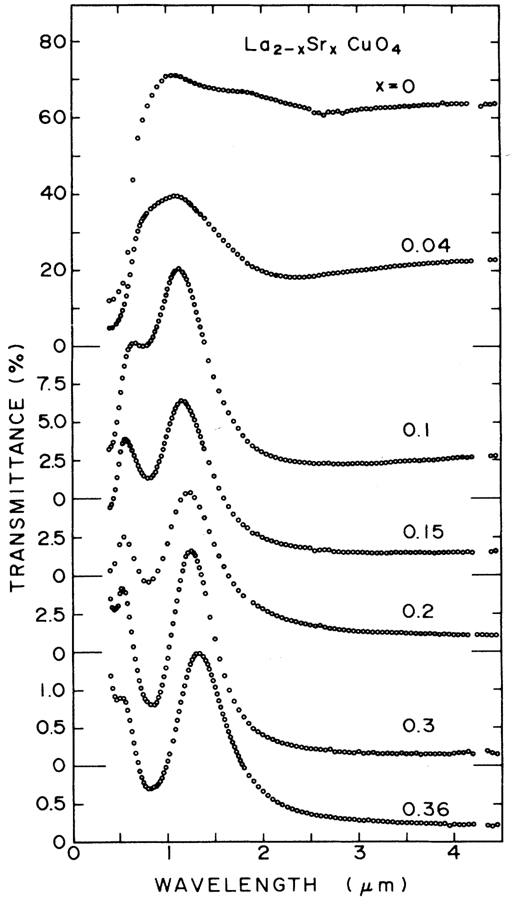

FIG. 11. Optical transmittance spectra for the La-Sr-Cu-O (001) epitaxial films with x from 0 to 0.36. Scales are shifted by appropriate values.

The most dramatic change with increasing x is the emergence of the additional absorption band centered at 0.85 μm. As x increases, the rise in $T(\lambda)$ shifts to shorter λ and, at the same time, the transmission peak splits into two, forming a broad absorption peak near 0.85 μm. With increasing x, the edge at longer λ shifts to lower energy, and at the same time the position of the absorption peak shifts slightly to lower energies, while its strength increases systematically with x. Ginder *et al.*[38] reported the existence of a band gap of about 2 eV in La_2CuO_4 based on their photoemission measurements. The present experiment directly confirms the band gap of La_2CuO_4 and, furthermore, suggests that the band gap persists when Sr ions are doped into this system. Ginder *et al.* also suggested the existence of two impurity levels within the band gap of La_2CuO_4, corresponding to 0.5 and 1.4 eV, respectively. In order to confirm the impurity level, the transmission measurements were performed on films with $x=0$ and 0.04, after they were reduced in an Ar atmosphere at 600 °C for 4 h or in vacuum of about 1×10^{-6} Torr for 4 h. However, no appreciable change in the transmission spectra was observed in either cases. This indicates that the oxygen vacancies are not basically responsible for the absorption peak centered at 1 μm. Furthermore, Shafer, Penny, and Olson[39] reported that the amount of oxygen vacancies for $x < 0.15$ is quite small, although it appears to increase for $x > 0.15$. In the present absorption spectra, the absorption band at 0.85 μm develops even for $x < 0.15$. Therefore, it is unlikely that the absorption at 0.85 μm is due to the oxygen vacancies.

At first glance, one simple interpretation of this absorption peak might be the electronic transition from the valence band to an impurity band about 1.6 eV high above E_F within the band gap. However, this is not likely for the following reasons. As the band calculation shows, the Sr ions at La sites do not seriously affect the electronic density of states near E_F. Furthermore, if the Sr ions are responsible for the impurity band, the edge of the absorption should shift to higher energies because E_F shifts to lower energies with Sr doping. This is contrary to the results shown in Fig. 11.

Since optical absorption is primarily determined by JDOS, it reflects both DOS's above E_F and the valence-band structure. From the above argument, it is reasonable that the change in the transmission spectra with Sr doping is caused by the dramatic change in the valence-band structure. The absorption coefficient $\alpha(\lambda)$, showing JDOS, is shown in Fig. 12. The magnitude of α at $\lambda = 0.85$ μm, where the absorption peak is centered, increases nearly proportionally with x. On the other hand, α at $\lambda = 0.4$ μm decreases when x increases from 0.04 to 0.15. This may indicate the reduction in DOS below E_F. Such a change in the valence-band DOS due to Sr doping was also observed by the EELS measurements.[15]

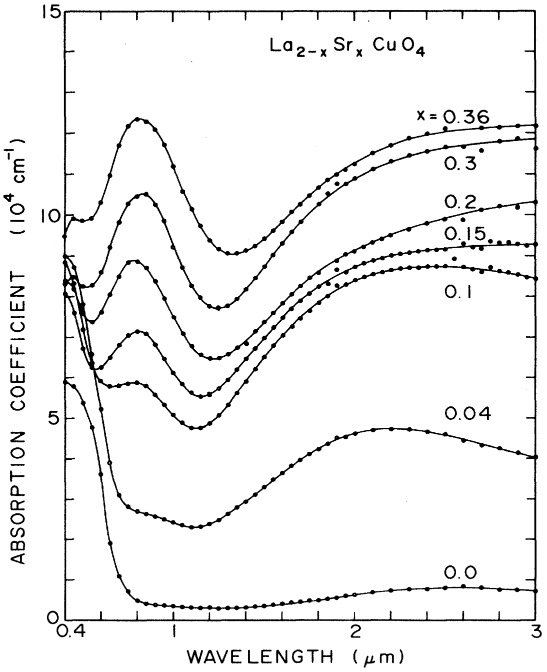

FIG. 12. Optical absorption coefficient α for the La-Sr-Cu-O epitaxial films with x from 0 to 0.36.

V. DISCUSSION

The primary interest of the present study is to clarify experimentally the electronic structure of the La-Sr-Cu-O system and its systematic change due to Sr doping. It is widely accepted that the undoped La_2CuO_4 is a charge transfer insulator rather than a Mott-Hubbard one.[14] In such a situation, the filled O $2p$ band lies slightly higher than or nearly at the same level as the lower Hubbard band. With Sr doping, holes are created in this O $2p$ band. This was experimentally confirmed. The x-ray photoemission spectroscopy measurements by Fujimori and co-workers[14,37] and the EELS experiment by Nücker *et al.*[15] showed that the carriers in the La-Sr-Cu-O and Ba-Y-Cu-O systems are holes on oxygens rather than on Cu ions. From the present study the optical mass ratio m^*/m of about or less than unity also reflects that the carriers are also p holes rather than d holes, in agreement with the experiments mentioned above. The systematic decrease in ρ and R_H means that the La-Sr-Cu-O system can be described basically by the band model and confirms the findings based on the Hall measurements on polycrystalline specimens by Ong *et al.*[16] Thus, it is quite reasonable that the La-Sr-Cu-O system changes from an insulator at $x = 0$ to a metal and the Fermi level shifts to lower energies from the valence-band top by the Sr doping, as far as the Hall effect is concerned.

Generally speaking, the Hall effect reflects the dynamics of electronic transport. In the low-field regime, the Hall effect is explained by the collision-dominated transport or in other words, electron scattering. In this case, because 7.7 kG in the present experiment corresponds to $B = 7.7 \times 10^{-5}$ V s/cm^2, $\mu B \ll 1$ is fulfilled. Even at $B = 12$ T, the inequality $\mu B \ll 1$ holds, and the results in Fig. 7 are in the low-field regime. As x increases, the La-Sr-Cu-O system becomes more metallic as mentioned above. It is not likely then that the decrease in R_H is caused by carrier localization at least in the superconducting composition region. Therefore, the temperature dependence of R_H seems to reflect the electronic scattering process. From this point of view, one should first pay attention to skew scattering by the local magnetic moments which interact with the conduction carriers through spin-orbital coupling. In order to put forth this idea, it is necessary that susceptibility $\chi(T)$ associated with the local magnetic moment has the same T dependence. However, there are few reports about the increase in $\chi(T)$ as T falls. This does not necessarily rule out the existence of local magnetic moments, because the amount of local magnetic moment should be very small due to the prevailing staggered spin fluctuation in this system. However, the results in Fig. 7 indicate that the interaction between conduction carriers and the local magnetic moment, if any, has a very slight effect on the scattering appearing in the Hall effect.

Another possible cause for the significant temperature dependence of R_H may be the coexistence of two types of carriers whose mobility exhibits strong T dependence. In this case R_H is expressed as $R_H = (\mu_p^2 n_p - \mu_n^2 n_n)/e(n_p\mu_p + n_n\mu_n)^2$. As Davidson, Santhanam, Palevski, and Brady[40] suggested, R_H can be T dependent if $n_p \approx n_n$ and the mobilities have such T dependence as

$|\mu_p - \mu_n| / |\mu_p + \mu_n| \propto 1/T$. In the case of Ba-Y-Cu-O system, where the chemical potential is considered to lie closely to the midband,[41] the above argument holds and the characteristics such as $R_H \propto 1/T$ can be expected. On the other hand, in the case of La-Sr-Cu-O system, the chemical potential may not reach the midband when $x < 0.4$. Therefore, the cancellation of n_n and n_p is not adequate, resulting in moderate temperature dependence compared with that of the Ba-Y-Cu-O system.

In a simple rigid-band model, R_H vanishes when the band is half-filled, and sign reversal occurs when E_F passes the midband. This agrees with the observed tendency where R_H decreases with x more rapidly than that expected from the Sr concentration. This leads to the idea that the change in R_H is closely related to the modified DOS near E_F. In the La-Sr-Cu-O system, R_H has a negative value when x exceeds 0.36, as inferred from Fig. 5. (Indeed, a negative R_H was observed for $x = 0.4$.) Assuming that the E_F is located in the lower Hubbard band, the midband corresponds to $x = 0.5$. However, this model seems to be inconsistent to the sign reversal in R_H which occurs near $x = 0.4$ rather than $x = 0.5$. One possible explanation is the shift of the DOS maximum toward the top of the valence edge.

As Nücker *et al.*[15] suggested, based on their local-density-functional band calculation, that Sr doping reduces DOS at 3–5 eV above E_F, which arises from La 5*d* and 4*f* states hybridized with O 2*p* states, and at the same time, increases the DOS near E_F, which comes from O 2*p* states. As a result, the Sr doping enhances the DOS of the O 2*p* band responsible for charge transfer excitation. It should be noted that the enhanced density of states comes from O ions in the Cu-O planes rather than LaO planes. It is reasonable that this enhanced density of states modifies or shifts the band, giving rise to the JDOS such as observed in the optical absorption in Fig. 12. The bandwidth of this enhanced DOS is estimated from Fig. 12 to be about 1 eV. Tajima *et al.*[33] estimated the bandwidth of the La-Sr-Cu-O system from the observed plasma frequency to be also about 1 eV. They found no candidate of this bandwidth in the band calculation results,[42] where the bandwidth is ~5 eV. However, the present experimental results correspond well to the estimation. If this enhancement of DOS near E_F is taken into account, the variation of ω_p with x, is not as simple as expected from a simple band model. However, the insensitiveness of ω_p to x, as observed in Fig. 10 and by Tajima *et al.*,[32] may probably be explained within this framework.

The change in the absorption coefficient in Fig. 12 implies two aspects of the band structure, of which the latter seems to have a rather interesting physical meaning. First, E_F shifts to lower energies from the band edge by doping, as discussed above. Second, the DOS is enhanced by doping, forming a band of about 1 eV in width. At the same time, the band gap, which was originally about 2 eV, decreases to about 1.2 eV. This is quite difficult to explain using a conventional band model. One possible cause for this reduction in the band gap can be found in the spin-bag mechanism proposed by Schrieffer, Wen, and Zhang.[13] In this model, the commensurate antiferromagnetic spin-density wave (SDW) causes a gap of ~1.7 eV. Introduction of a hole reduces antiferromagnetic order inside the domain, causing local suppression of the SDW gap. This may be reflected in the optical absorption spectrum as the reduction of the optical gap, as just observed in the present study. Indeed the optical density at this reduced energy, which may be proportional to the number of spin-bags, increases nearly proportionally to the hole concentration.

Finally, the following should be noted. Concerning the anomaly in the DOS in the valence band top, Fujimori *et al.*[37] pointed out that in the cuprate superconductors there should be a Kondo peak at the top of the valence band near E_F. This peak rises through the hybridization of the 3*d* electrons and the 2*p* electrons. Although it was not shown clearly, the EELS measurements by Nücker *et al.* for both the La-Sr-Cu-O and Ba-Y-Cu-O systems revealed that there is a peak of DOS near E_F, the width of which is comparable to the present experimental results.

VI. CONCLUSION

From the systematic measurements of the Hall coefficient, optical reflectance and transmittance for the La-Sr-Cu-O single-crystal thin films with various x, it is found that the electronic structure of the La-Sr-Cu-O system and the transport within the Cu-O planes are well described basically by a band model. Sr doping causes significant enhancement in DOS near E_F, forming a band of ~1 eV width which comes from O 2*p* states. It also reduces the band gap from ~2 to ~1.2 eV. The decrease in the Hall coefficient with increasing x is due to the shift of E_F to lower energies from the top of this band, and even the faster decrease in the Hall coefficient at $x > 0.2$ is explained by the shift of band maximum by this enhancement. The temperature dependence of the Hall coefficient is likely to be caused by two types of carriers having significant temperature dependence rather than by scattering due to the localized magnetic moments which are likely to exist in this system.

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