Filling Dependence of Electronic Properties on the Verge of Metal–Mott-Insulator Transitions in $Sr_{1-x}La_xTiO_3$

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Introducing holes (or partly eliminating electrons) in Mott-Hubbard insulator $LaTiO_3$ (with $3d^1$ configuration) can be carried out by partial substitution of La with Sr, which produces the strongly correlated metallic phase. Systematic variation of electronic properties in $Sr_{1-x}La_xTiO_3$ was investigated as a function of the $3d$ band filling (x) by measurements of resistivity, Hall coefficient, magnetic susceptibility, and specific heat. Up to the vicinity of the metal-insulator phase boundary ($x_c \sim 0.95$), $Sr_{1-x}La_xTiO_3$ behaves as a Fermi liquid system where the carrier mass and scattering rate critically increase as the $x=1$ ($LaTiO_3$) insulator is approached.

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Stimulated by discovery of high-T_c superconductivity, electronic structures and properties in strongly correlated electron systems have been attracting renewed attention. Ternary or multinary oxides of transition metals are of particular interest, since the chemical potential or the filling of the narrow d electron band can be controlled by chemical substitution (e.g., at the A sites of the perovskite structure) while keeping fundamental metal-oxygen networks. The layered cuprate compounds with high-T_c superconductivity are prototypes for such filling-controlled materials [1] with strong electron correlations. By changing the effective valence of Cu or filling of the Cu-O related band, the cuprate compounds undergo the phase change from the insulator to high-T_c superconductor (or unconventional metal above T_c). According to the Zaanen-Sawatzky-Allen scheme [2], the parent cuprates are classified as the charge-transfer (CT) insulators where the charge gap is formed between the occupied O $2p$ states and unoccupied Cu $3d$ states (upper Hubbard band). On the other hand, there are ample examples of insulating transition metal oxides [3] (Mott insulators in a narrow sense), where the possible charge gap is formed between the Coulomb-split d bands (i.e., lower and upper Hubbard bands). One of the most extensively investigated compounds is V_2O_3 (Refs. [3,4]) with a $3d^2$ configuration of V, which undergoes the metal-insulator transition by applying pressure, changing oxygen stoichiometry, or alloying with Ti_2O_3. However, the control of the band filling in the binary systems (e.g., V_2O_3) is limited near the stoichiometric composition, since a heavy alloying at the transition metal sites or large nonstoichiometry inevitably introduces the randomness into the system. Apart from the studies on the finely valence-controlled V_2O_3 (Ref. [4]), there have been very few careful studies on the systematic change of electronic properties upon the Mott-insulator–metal transition which is driven by change of filling or by "carrier doping."

The purpose of this Letter is to report on systematic variation of electronic and magnetic properties from changing the band filling in strongly correlated metals on the verge of the Mott-Hubbard transition. The system we have investigated is the newly synthesized solid solution system, $Sr_{1-x}La_xTiO_3$ with perovskite-like structure, in which a number of $3d$ electrons can be varied from 0 to 1 with a change of x from 0 ($SrTiO_3$) to 1 ($LaTiO_3$). The end compound $LaTiO_3$ ($x=1$), when well stoichiometric, has been known to show nonmetallic behavior [5] due to electron correlation and the antiferromagnetic ordering of Ti $S=\frac{1}{2}$ spins at $T_N=120$–150 K [5,6]. However, the insulating state associated with the magnetically ordered phase is easily broken and transformed to the metallic state with a slight increase (≥ 0.05) of the Ti valence from $+3.0$ ("hole-doping" procedures) by La/O off-stoichiometry or by Sr doping onto the La sites [5–8]. Furthermore, the Ti sites form a nearly simple cubic lattice in such a perovskite-related crystal, which is expected to show almost isotropic electronic properties. Therefore, $Sr_{1-x}La_xTiO_3$ may be one of the most desirable systems in which critical dependence of physical parameters on the band filling can be investigated in the vicinity of the Mott-Hubbard transition. The behavior near the metal-nonmetal phase boundary in the "hole-doped" Mott system is of particular interest in comparison with the case of high-T_c cuprates.

Samples of $Sr_{1-x}La_xTiO_3$ were melt grown in a reducing atmosphere by the floating zone method, details of which were reported previously [8]. Special attention was paid to synthesis of the samples with x close to 1 including the sample $LaTiO_3$, since even a slight off-stoichiometry will change electronic properties near the metal-nonmetal phase boundary [5-8]. Careful precalcining of La_2O_3 (source of La) and a fairly strong reducing condition (40% H_2/Ar) prevented the La deficiencies and extra oxygen. The presently prepared $LaTiO_3$ shows a nonmetallic behavior over all temperatures below 300 K, as shown in the inset of Fig. 1, with $T_N = 138$ K. Thermogravimetric analysis showed the effective Ti valence of 3.02 for the insulating $x = 1$ sample and the oxygen off-stoichiometry less than 2% of the total oxygen content for the Sr-substituted samples. The insulating state in $LaTiO_3$ was confirmed to be amenable to the hole-doping procedure by the partial substitution with Sr as seen in the metallic behavior (the inset of Fig. 1) of $Sr_{0.05}La_{0.95}TiO_3$ ($x = 0.95$).

Temperature dependence of the resistivity (ρ) in metallic compounds $Sr_{1-x}La_xTiO_3$ is shown in Fig. 1, where $\rho - \rho_0$ is plotted against the square of the temperature (T^2). The residual resistivity ρ_0 in the metallic compounds is ca. 2×10^{-4} Ω cm for the $x = 0.5$ sample and $(5\text{-}7) \times 10^{-4}$ Ω cm for $0.6 \leq x \leq 0.95$. The metallic behavior persists in the samples with the lower filling of $x < 0.5$ (not shown in the figure), yet the samples with $x \leq 0.1$ show some carrier localization effect [7], perhaps due to poor shielding of the impurity (La^{3+}) potential by low carrier density. Notably, the temperature dependencies of resistivity in the metallic region are well characterized by the relation $\rho = \rho_0 + AT^2$, over a wide temperature region (at least up to 200 K). The quadratic temperature dependence of resistivity is reminiscent of the strong electron-electron scattering process which seems to predominate the electron-phonon scattering process. The coefficient A increases conspicuously with filling as the $x = 1$ Mott insulator is approached in spite of comparable values of ρ_0. Such a filling-dependent behavior signals a systematic change of the scattering rate and the effective mass of carriers (*vide infra*). Incidentally, the increase in the T^2 coefficient of the resistivity as the metal-insulator transition is approached has also been observed in V_2O_3 (Ref. [9]) where pressure rather than the filling control was used to drive the system through the transition.

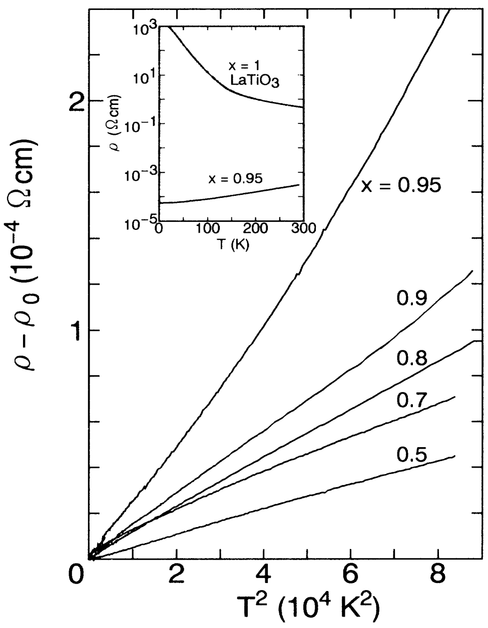

FIG. 1. Temperature (T) dependence of resistivity (ρ) in $Sr_{1-x}La_xTiO_3$. ρ is plotted vs T^2. The inset shows ρ vs T plots in the nonmetallic $x = 1$ ($LaTiO_3$) and metallic $x = 0.95$ samples.

To estimate the carrier concentration and its filling dependence in $Sr_{1-x}La_xTiO_3$, we have measured the Hall coefficient. The inverse of the Hall coefficient R_H^{-1} is plotted against x in Fig. 2. In the metallic region, at least for $0.1 \leq x \leq 0.95$, the Hall coefficient was observed to be negative (i.e., of electron type) and nearly temperature independent as exemplified by respective values measured at 80 K (closed circles) and 173 K (open circles) in Fig. 2. The absolute value of R_H^{-1} varies linearly with x up to at least $x = 0.95$. Thus estimated carrier density as a function of x is in excellent agreement with the simple prediction (indicated by a straight line) assuming that each substitution of a Sr^{2+} site with La^{3+} supplies one electron-type carrier per Ti site. [The change of unit cell volume $Sr_{1-x}La_xTiO_3$ is small (less than 4%) and may be neglected in the following discussion.] In other words, the 3d band filling x gives a previse measure of the carrier density in the metallic phase of $Sr_{1-x}La_xTiO_3$ even in the composition region close to the insulating end ($x = 1$). The observed behavior implies existence of the Fermi surface which satisfies the Luttinger sum rule. In particular, in the metallic region near $x = 1$, the compound must show a large Fermi surface as expected for the noninteracting electrons and *not* the small one typical for holes doped in the insulator. The simple behavior of

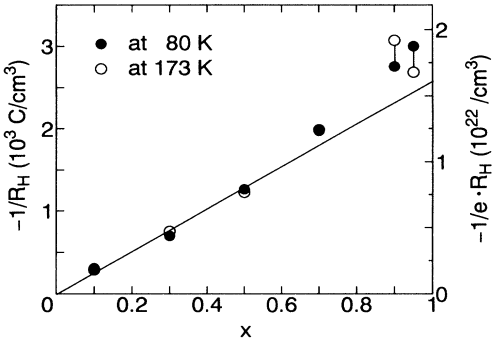

FIG. 2. The filling (x) dependence of the inverse of Hall coefficient (R_H^{-1}) in $Sr_{1-x}La_xTiO_3$. Open and closed circles represent the values measured at 80 K and 173 K, respectively. A solid line indicates the calculated one based on the assumption that each substitution of a Sr^{2+} site with La^{3+} supplies the compound with one electron-type carrier per Ti site.

R_H observed in $Sr_{1-x}La_xTiO_3$ implies that the Fermi liquid picture [10] may be applied up to the verge of the metal-insulator transition in this three-dimensional system. The observed filling dependence of R_H in $Sr_{1-x}La_xTiO_3$ is in contrast with the case of hole-doped layered cuprate compounds, e.g., $La_{2-x}Sr_xCuO_4$, where the Hall coefficient remains positive in the region of $0<x<0.2$ (or the filling range, $0.8<1-x<1.0$) [11].

That the system verges on the metal-insulator transition with x manifests itself in other measurable quantities. In Fig. 3 we show x variation of the T linear slope (γ) of electronic specific heat in $Sr_{1-x}La_xTiO_3$ by closed circles. The heat capacity (c) in the sample was measured by the adiabatic heat pulse method with a calibrated Ge thermometer. The values of γ could be unambiguously determined from the well-defined intercepts of the c/T vs T^2 plots which show straight lines without any upturn or downturn behavior as $T\to 0$. Then, the renormalized density of states at the Fermi level $N(E_F)$ can be deduced using the relation $\gamma=(\pi^2/3)k_B^2N(E_F)$. As is evident in the figure, $N(E_F)$ in $Sr_{1-x}La_xTiO_3$ increases with x and shows a critical enhancement as the end ($x=1$) insulator is approached.

Spin susceptibility (χ) data at 300 K in the metallic phase are also plotted in Fig. 3 by open circles. (The contribution due to the core diamagnetism was subtracted from the raw data of magnetic susceptibility.) χ in the metallic phase is nearly temperature independent typical of Pauli paramagnetism. It is remarkable that data of both γ and χ show quite a parallel behavior. In fact, the Wilson ratio (χ/γ in units of $3\mu_B^2/\pi^2k_B^2$) is nearly constant (~ 2) against x, as shown in the upper part of Fig. 3. The results indicate absence of Stoner enhancement even when the system approaches the Mott insulator with increase of x. This may be in accord with the Brinkman-Rice picture [12] for the half-filled Hubbard model.

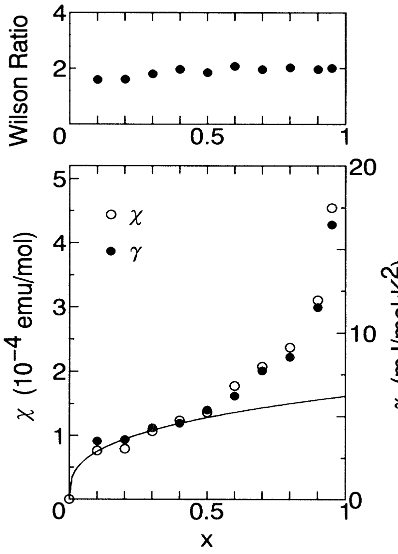

FIG. 3. The filling (x) dependence of the T linear coefficient of low-temperature specific heat (γ, closed circles) and nearly temperature-independent spin susceptibility (χ) at 300 K (open circles). In the upper part, the Wilson ratio, χ/γ normalized by $3\mu_B^2/\pi^2k_B^2$, is plotted vs x.

According to the Fermi liquid model (FLM) [13], γ and χ can be expressed by the relations

$$\gamma=(m^*/m_B)\gamma^{(0)}$$

and

$$\chi=(m^*/m_B)\chi^{(0)}/(1+F_0^a)\,.$$

Here, m_B, $\gamma^{(0)}$, and $\chi^{(0)}$ represent the respective values for a noninteracting electron system and F_0^a the standard notation of the Landau parameter [13]. In the case of the isotropic (spherical) Fermi surface, $\rho^{(0)}$ for the noninteracting system (and hence both of $\gamma^{(0)}$ and $\chi^{(0)}$) scale(s) with the filling such as $\propto x^{1/3}$. A solid line shown in Fig. 3 represents the reference for $x^{1/3}$. Deviation of the observed $N(E_F)$ from this reference line becomes readily appreciable above $x=0.5$ and increases with x as the Mott insulator ($x=1$) is approached. This is in contrast with the fact that the Hall coefficient (R_H) shows the filling dependence ($\propto x^{-1}$) which is identical with the uncorrelated case. In terms of FLM the filling-dependent increase of γ and χ is ascribed to enhancement of the effective mass m^* of correlated electrons [13]. [In this case, F_0^a must be nearly constant (~ -0.5) against the filling x.] The critical mass enhancement as observed is obviously due to the effect of electron correlation which becomes significant with x and causes the Mott-Hubbard-type insulation at the end ($x=1$) filling. In other words, the barely metallic behavior near $x=1$ is characterized not by decrease of the carrier density but by increase of the effective mass (and perhaps also the scattering rate) of carriers.

The enhancement of m^* with the band filling in strongly correlated electron systems has been theoretically asserted on the basis of the exact solution of the one-dimensional Hubbard model [14] and numerical studies on the two-dimensional Hubbard model [15] as well as the slave boson approach for the three-band (Cu-O plane) Hubbard model [16]. To the best of our knowledge, however, the present result is the first *experimental* confirmation of such a critical behavior for the real three-dimensional Mott-Hubbard system. The theories [13,14] have predicted the critical behavior that $m^*\propto(1-x)^{-1}$. The observed enhancement of m^* above $x=0.6$ appears not to be as steep as by the theoretical predictions for the one- or two-dimensional Hubbard model.

Keeping the above in mind, we may argue the transport data shown in Fig. 1 in terms of FLM. The effect of electron correlation also causes the increase of the scattering rate of quasiparticles near E_F. For a large class of metals with strong correlation, in particular

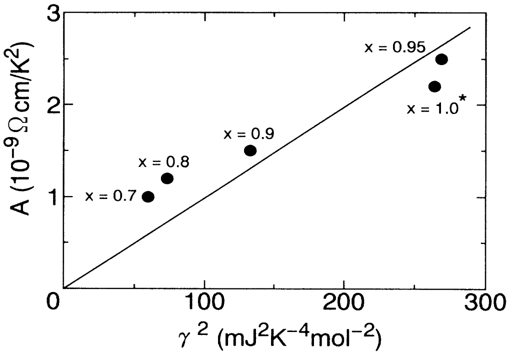

FIG. 4. The T^2 coefficient of resistivity (A) plotted vs the square of the T linear coefficient of low-temperature specific heat (γ^2) for the metallic $Sr_{1-x}La_xTiO_3$ near the metal-nonmetal phase boundary ($x \geq 0.7$). The notation $x = 1^*$ indicates the nominally $x = 1$ sample which is barely metallic perhaps due to a slight amount (ca. 2%) of La deficiencies.

heavy fermion systems, the empirical relation that $A \propto \gamma^2$ has been reported to hold well [17,18]. In Fig. 4 we have plotted A against γ^2 for several samples of $Sr_{1-x}La_xTiO_3$ near the metal-insulator phase boundary. As expected, the above relation that $A \propto \gamma^2$ holds approximately also in this system, which again ensures that the steep increase of A in resistivity with x originates from the strong electron correlation on the verge of Mott-Hubbard transition. It is worth noting that the A/γ^2 ratio [ca. 1.0×10^{-11} Ωcm (mol K/mJ)^2] observed in the present titanate compounds agrees quite well with the universal value reported for the heavy fermion system [17], though γ values for the latter are larger by 1 or 2 orders of magnitude than those for the present system. This may signal an underlying common mechanism for the constant A/γ^2 ratio in these strongly correlated electron systems [18].

In conclusion, we have investigated the filling (x) dependence of the metallic properties in $Sr_{1-x}La_xTiO_3$ with strong electron correlations. With the A-site substitution in the perovskite-like ternary system, we could comprehensively investigate a systematic behavior of electronic properties over a wide range of the band filling, which would be difficult with the use of the binary oxide systems (e.g., Ti_2O_3 and V_2O_3). Up to the vicinity of the metal-Mott-insulator phase boundary, the behavior can be well described by the Fermi liquid model. The effective mass of carriers is critically enhanced by the effect of electron correlation as the end Mott insulator is approached. Such a mass enhancement effect has also shown up in the optical spectra [8]: As the compound approaches the $x = 1$ insulator, the plasma frequency $[\propto (x/m^*)^{1/2}]$ has been observed to be conspicuously suppressed, indicating again the critical increase of m^*. Therefore, the metal-nonmetal phase transition in this system may be characterized by divergence of effective mass of carriers. The Fermi-liquid-like behavior up to the vicinity of the metal-insulator phase boundary observed in these titanates is contrasted by a filling-dependent behavior of the unconventional normal-state properties of high-T_c cuprates. The difference may come from the dimensionality (3D vs 2D) or more likely from the nature and magnitude of the charge gap in the parent insulators (the charge-transfer-type gap of 1.5-2 eV [19] for the CuO_2-layered compounds and the Mott-Hubbard gap of ca. 0.1 eV [6] for $LaTiO_3$).

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[1] For a review on the filling control in layered cuprate compounds, see, for example, Y. Tokura and T. Arima, Jpn. J. Appl. Phys. **29**, 2388 (1990).
[2] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).
[3] For a review, see *The Metallic and Non-Metallic States of Matter,* edited by P. P. Edwards and C. N. R. Rao (Talor & Francis, London, 1985).
[4] S. A. Carter, T. F. Rosenbaum, J. M. Honig, and J. Spalek, Phys. Rev. Lett. **67**, 3440 (1991), and, references cited therein.
[5] F. Lichtenberg, D. Widmer, J. G. Bednorz, T. Williams, and A. Reller, Z. Phys. **B82**, 211 (1991).
[6] D. A. Crandles, T. Timusk, and J. E. Greedan, Phys. Rev. B **44**, 13250 (1991); D. A. Crandles, T. Timusk, J. D. Garrett, and J. E. Greedan, Physica (Amsterdam) **201C**, 407 (1992).
[7] Y. Maeno, S. Awaji, H. Matsumoto, and T. Fujita, Physica (Amsterdam) **165-166B**, 1185 (1990).
[8] Y. Fujishima, Y. Tokura, T. Arima, and S. Uchida, Phys. Rev. B **46**, 11167 (1992).
[9] D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman, and T. M. Rice, Phys. Rev. B **7**, 1920 (1973).
[10] J. Spalek, J. Solid State Chem. **88**, 2 (1990).
[11] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989).
[12] W. F. Brinkman and T. M. Rice, Phys. Rev. B **2**, 4302 (1970).
[13] D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).
[14] M. Kawakami and S.-K. Yang, Phys. Rev. Lett. **65**, 2309 (1990).
[15] N. Furukawa and M. Imada, J. Phys. Soc. Jpn. **60**, 3604 (1991).
[16] C. A. R. Sá de Melo and S. Doniach, Phys. Rev. B **41**, 6633 (1990).
[17] K. Kadowaki and S. B. Woods, Solid State Commun. **58**, 507 (1986).
[18] K. Miyake, T. Matsuura, and C. M. Varma, Solid State Commun. **71**, 1149 (989).
[19] Y. Tokura *et al.*, Phys. Rev. B **41**, 11657 (1990); S. L. Cooper *et al.*, Phys. Rev. B **42**, 11605 (1990).