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Change of electronic properties on the doping-induced insulator-metal transition in $La_{1-x}Sr_xVO_3$

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Changes in electrical, magnetic, and optical properties have been investigated for the doping-induced insulator-metal (I-M) transition in hole-doped Mott insulators, $La_{1-x}Sr_xVO_3$. In the optical spectra, the I-M transition is characterized by doping-induced transfer of spectral weight into the in-gap region. Resistivity in the metallic phase near the critical magnetic phase boundary shows such a temperature dependence as expressed by the relation $\rho=\rho_0+AT^{1.5}$ over a wide temperature range (2–200 K) with the enhanced coefficient A towards the phase boundary. The results are argued in terms of effect of the antiferromagnetic spin fluctuation on the charge transport.

Renewed interest in the electronic properties of $3d$ transition metal oxide compounds with strong electron correlation has been aroused by the discovery and subsequent extensive studies of high-temperature (high-T_c) superconducting cuprates. $LaVO_3$ and its hole-doped analogs $La_{1-x}Sr_xVO_3$, as well as V_2O_3 and related compounds, have long been known as a system which shows the insulator-metal (I-M) transition relevant to the strong electron correlation effect similarly to the case of the high-T_c cuprates. Recent studies on the high-T_c cuprates have shown the necessity of comprehensive investigation on the interplay between the spin and charge dynamics with the case of finely filling-controlled samples. Here, we update the results of the electronic properties and their filling dependence for $La_{1-x}Sr_xVO_3$ using melt-grown polycrystals. We have found a conspicuous change in conductivity spectra, i.e., the collapse of the Mott gap and resultant spectral weight transfer, in the present vanadate system which is to be compared with the case of the hole-doped cuprate and titanate systems.[1–3] The charge transport in a barely metallic state near the I-M phase boundary ($x=0.2$ of $La_{1-x}Sr_xVO_3$) appears to be strongly affected by antiferromagnetic spin fluctuation and shows a non-Fermi-liquid-like behavior.

The parent compound $LaVO_3$ is one of prototypical Mott insulators with the electron configuration of $3d^2$ and undergoes a magnetic phase transition to a weakly ferromagnetic state with essentially antiferromagnetic spin ordering below $T_N=140$ K.[4,5] The other end compound $SrVO_3$ with configuration of $3d^1$ is a good metal[6] perhaps due to the large d electron transfer interaction mediated with strong hybridization between V $3d$ and O $2p$ states. This is in contrast with similar $3d^1$ perovskites of a Ti^{3+}-based oxide, e.g., $LaTiO_3$, which are all Mott insulators.[7,8] The solid solution $La_{1-x}Sr_xVO_3$ can be formed over the whole composition region ($0\leq x\leq 1$).[9] The nominal hole doping by substitution of Sr for the La site causes an insulator-metal (I-M) transition around $x=0.2$.[9–11] The Seebeck coefficient in the insulating or semiconducting region below $x=0.2$ was reported to be positive, indicating the hole-type conduction.[10] At low temperatures of the insulating phase, antiferromagnetic phase appears to survive up to the I-M phase boundary. On the other hand, the Hall coefficient for $x>0.3$ is negative and small in magnitude ($R_H=-2\times10^{-4}$ cm^3/C for $x=0.4$),[12] which is typical of a metal. However, little has been known about the interplay between the charge transport and spin dynamics in the immediate vicinity of the I-M transition in this compound, which is in contrast with the famous case of V_2O_3.[13]

Polycrytalline powder of $La_{1-x}Sr_xVO_3$ was first prepared by a solid state reaction of starting compounds, V_2O_5, La_2O_3, and $SrCO_3$ at 1300 °C in flow of a forming gas of Ar/H_2 (93/7%). Firing and grinding procedures were repeated several times. Then, the powder was pressed into pellets and melted under Ar atmosphere with a tri-arc furnace. Several specimens were further annealed at 1200 °C for 90 h in flow of Ar/H_2 (93/7%) gas.

Thermogravimetric analysis (TGA) was performed to check the possible oxygen nonstoichiometry. The oxygen nonstoichiometry δ ($La_{1-x}Sr_xVO_{3+\delta}$) was determined by assuming that the perovskite A-site composition (La/Sr) coincided with the prescribed stoichiometry and that the product of the TGA procedure (heating the sample to 1000 °C in oxygen gas flow) contained only V^{5+}. The results are shown in Table I together with observed critical temperature (T_N) for the antiferromagnetic spin order (*vide infra*). The specimens appear to contain excess oxygen, in particular, for the

TABLE I. Oxygen stoichiometry (δ) and the magnetic phase transition temperature (T_N) of the samples of $La_{1-x}Sr_xVO_{3+\delta}$ prepared by the arc-melting method in the present study.

x	$3+\delta$	T_N (K)
0	3.044	144
0.05	3.071	126
0.10	3.024	110
0.15	3.059	95
0.20	3.025	75
0.22	2.994	20
0.25	3.022	
0.28	3.012	
0.30	3.032	
0.40	3.028	
0.50	3.046	

low-x samples and such a tendency is in accord with the results that were previously reported by Mahajan *et al.*[5] on the similarly arc-melt samples. Therefore, the nominal hole number should be shifted higher than the Sr content x. However, we present the following experimental results as a function of x and not of the actual hole number involving the oxygen nonstoichiometry since the above estimation of δ is supposed to contain a considerable systematic error for the moderately Sr-doped samples; perhaps $\delta = \pm 0.01$ according to the experience of the TGA on the different specimens with the identical x and similar electronic properties. We have prepared a series of samples under the same atmosphere and the same procedure and, in fact, the observed behaviors of electronic and magnetic properties are systematic with x and the discussion in terms of x may be valid at least for the critical behavior of the insulator-metal transition.

Powder x-ray diffraction patterns showed that the lattice structure for $0 \leqslant x \leqslant 0.20$ is pseudotetragonal and that for $x \geqslant 0.30$ rhombohedral at room temperature. The change of the main phase was observed to occur around $x = 0.22$, which is in accord with the literature.[9,10] However, a faint tetragonal distortion is observed in the powder patterns of the presently prepared compounds with $x = 0.22$, 0.25, and 0.28 as traces of additional diffraction peaks. This may be partly due to local inhomogeneity of the composition. However, it is difficult at the present stage to avoid such a slight phase mixture, since the phase transition between the two structural phases is of the first order and both phases are perhaps nearly degenerate in free energy in the composition region of $x = 0.2$–0.3.

Resistivity measurements were performed on the specimen of a rectangular shape (typically $3 \times 2 \times 1$ mm^3) by the four-probe method. The electrical contacts were made with indium which was soldered ultrasonically. Magnetization was measured with a commercial superconducting quantum interference device magnetometer. To detect magnetic ordering at low temperatures, the sample was first field cooled under a magnetic field of 5 T and then the magnetization was measured in a field-warming run with a relatively small field (10 mT). The antiferromagnetic ordering in the insulating samples shows weak ferromagnetism due to spin canting, and hence can be detected as a small ferromagnetic magnetization. The temperature at which the weak-ferromagnetic magnetization disappears was adopted as the critical temperature (T_N) for the antiferromagnetic spin order.

Optical reflectance measurements were performed in the photon energy range of 0.05–30 eV at room temperature. For the energy region below 0.5 eV a Fourier transform spectrometer was used, while the grating spectroscopy was used above 0.5 eV. For the photon energy region above 5 eV, we utilized synchrotron radiation at the INS-SOR, Institute for Solid State Physics, University of Tokyo. Spectra of optical conductivity were obtained by the Kramers-Kronig analysis, in which the reflectivity was assumed to be constant in the energy ($\hbar\omega$) region below 0.05 eV and to vary as ω^{-4} above 30 eV. The data in the higher energy region (to be published elsewhere) are not presented in this paper, but were useful to obtain accurate spectra of the optical conductivity in the lower-energy region.

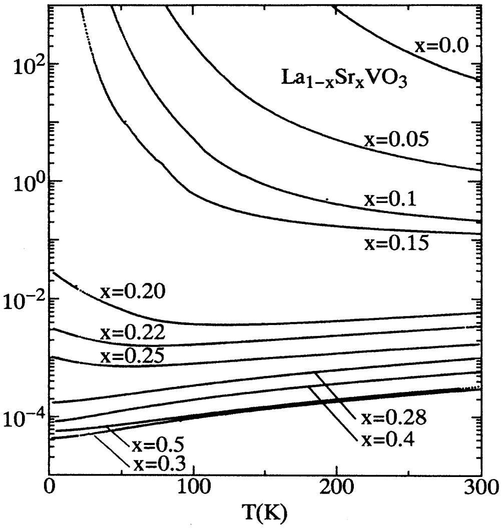

FIG. 1. Temperature dependence of resistivity in La$_{1-x}$Sr$_x$VO$_3$.

Figure 1 shows temperature dependence of resistivity in La$_{1-x}$Sr$_x$VO$_3$. An *I-M* transition appears to take place around $x = 0.20$, which is in accord with the results of previous studies.[9–11] However, the resistivity of the samples in the immediate vicinity of the *I-M* phase boundary, such as the $x = 0.20$, 0.22, and 0.25 samples, shows an upturn below 100 K. In these composition and temperature regions, there seems to be a close interplay among the antiferromagnetic spin fluctuation, the localization effect from the random potential, and the crystallographic phase change. As shown later, the antiferromagnetic ordering of spins persists up to $x = 0.22$ in our samples (see Table I).

The doping-induced *I-M* transition and the resultant drastic change of the electronic structure show up clearly in optical spectra. Figure 2 shows low-energy parts of the optical conductivity spectra at room temperature for La$_{1-x}$Sr$_x$VO$_3$

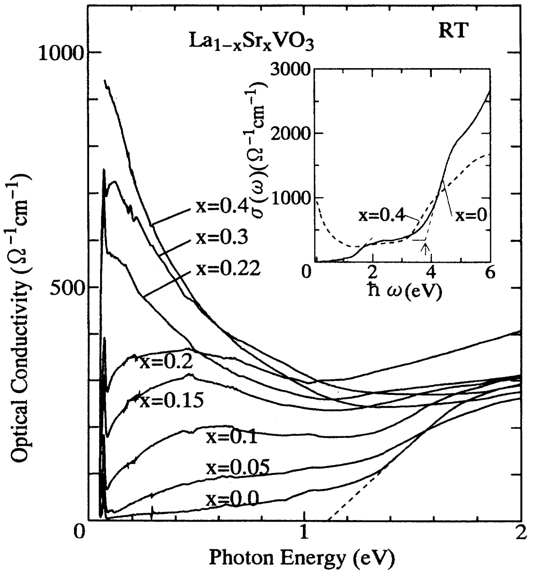

FIG. 2. Spectra of optical conductivity at room temperature in La$_{1-x}$Sr$_x$VO$_3$.

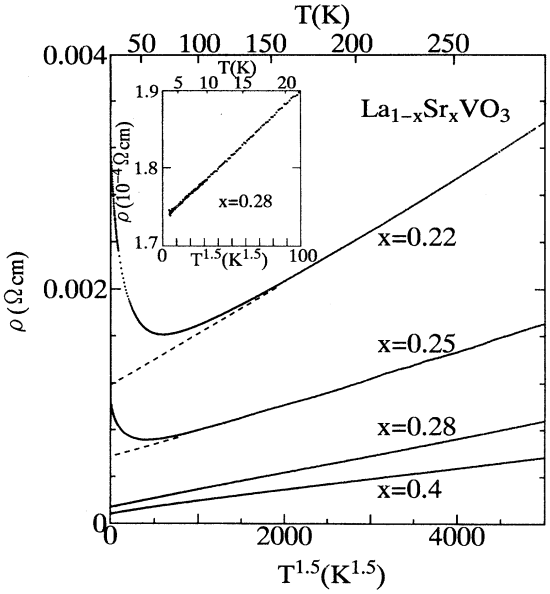

FIG. 3. Temperature (T) dependence of resistivity (ρ) for the samples of $La_{1-x}Sr_xVO_3$ near the insulator-metal phase boundary. ρ is plotted against $T^{1.5}$.

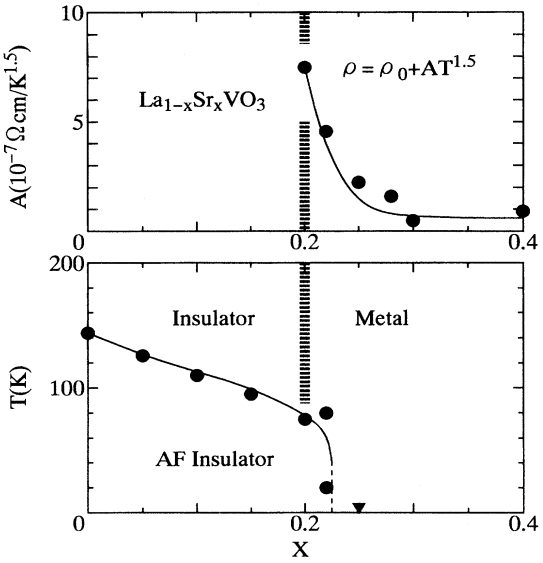

FIG. 4. The x dependence of the coefficient A (upper panel), that is the slope of the resistivity (ρ) vs $T^{1.5}$, and the electronic phase diagram (lower panel) for $La_{1-x}Sr_xVO_3$.

together with the inset for a broader energy region. In $LaVO_3$ a Mott-Hubbard gap between the lower and upper Hubbard bands (V $3d$ bands) and a charge-transfer (CT) gap between the occupied O $2p$ band and the upper Hubbard band are observed at 1.1 eV and 3.6 eV, respectively,[14] as discerned as rises of the optical conductivity shown in the inset. With nominal hole doping by the Sr substitution (x), the CT gap shifts to lower energy mainly due to the shift of the $2p$ band[15] and the Mott-Hubbard gap is closed, as shown for the case of the $x=0.3$ sample in the inset. As for the doping-induced change in the low-energy region (Fig. 2), the spectral weight is first increased in the gap region and eventually forms a so-called in-gap absorption band. For example, the low-energy conductivity spectra for the barely metallic samples with $x=0.20$ and 0.22 show a non-Drude behavior, implying dominant contribution from the incoherent motion of the charge carriers. By contrast, the spectra for $x\geqslant 0.3$ are Drude-like as in conventional metals. As compared with the case of the related compound $Y_{1-x}Ca_xVO_3$,[15] the doping-induced change takes place at a lower hole-doping level, in accord with the difference in the critical compositions of the I-M transition, $x=0.2$ for the present case and $x=0.5$ for $Y_{1-x}Ca_xVO_3$. Such a change of the optical conductivity spectrum in the course of the I-M transition is a generic feature for the strongly correlated electron systems, in particular, for filling-controlled $3d$ transition metal oxides such as the doped copper oxides and titanium oxides.[1–3]

Thus the inner-gap states are responsible for the low-energy electronic structures in the immediate vicinity of the I-M phase boundary. In such a critical region, the charge transport appears to also show an anomalous behavior. We show in Fig. 3 the resistivity of the compounds near the I-M phase boundary as a function of $T^{1.5}$. Apart from the upturns at low temperatures for the $x=0.22$ and $x=0.25$ samples, temperature dependence of resistivity (ρ) can be well expressed by the relation $\rho=\rho_0+AT^{1.5}$ in the metallic region near the I-M phase boundary. The inset of Fig. 3 shows magnification of the low-temperature region for the $x=0.28$ sample, indicating that the above relation holds good at least down to 2.5 K.

In the upper panel of Fig. 4 we show the x dependence of the coefficient A, that is the slope of the resistivity to $T^{1.5}$, together with the electronic phase diagram (the lower panel). The antiferromagnetic ordering disappears around $x=0.22$ near the I-M phase boundary. Comparing the magnetic phase diagram with the temperature dependence of the resistivity in Fig. 1, there seems to be an antiferromagnetic metal phase in the narrow composition region of $0.20\leqslant x\leqslant 0.22$, with a positive temperature gradient of the resistivity $d\rho/dT$ below T_N. However, the conclusion about the presence of the antiferromagnetic *metal* phase in $La_{1-x}Sr_xVO_3$ should be postponed until the study on a better quality of samples (say, single crystals). The coefficient A appears to be remarkably enhanced as the system approaches from the metallic side to the insulating region with decrease of x.

The self-consistent renormalization theory by Moriya and co-workers[16–18] indicates that the low-temperature resistivity at the critical boundary between the antiferromagnetic metal and normal metal deviates from a normal T^2 law and shows $T^{1.5}$ dependence. The $T^{1.5}$ dependence observed down to low temperature for the $x=0.28$ sample (see the inset of Fig. 3) may reflect such a non-Fermi-liquid-like behavior at the phase boundary. The $T^{1.5}$ dependence of the resistivity is interpreted in terms of the strong Curie-like enhancement of the spin susceptibility at the antiferromagnetic wave vector, $\chi(\vec{Q})$, since the temperature dependence of the resistivity in the strong spin fluctuation region can be expressed as

$$\rho(T)=\rho_0+AT^2,$$

where

$$A \propto \sqrt{\chi(\vec{Q})}$$

for the three-dimensional case.[19] The Curie-Weiss-like behavior such as

$$\chi(\vec{Q}) = \frac{C}{T+T_0}$$

may be expected for nearly antiferromagnetic metals such as $La_{1-x}Sr_xVO_3$. Here, the *Weiss temperature* T_0 tends to vanish at the critical boundary, which may lead to $T^{1.5}$ dependence of the resistivity as observed. To confirm the present scenario, the strong antiferromagnetic spin fluctuation should be detected by other probes, such as NMR and neutron inelastic scattering, near the critical boundary, namely, in the region of $x=0.20$–0.25 for the case of $La_{1-x}Sr_xVO_3$.

In conclusion, we have observed the conspicuous change of the low-energy electronic structure with hole doping (x) in the doped Mott insulator compounds $La_{1-x}Sr_xVO_3$. The barely metallic state in the immediate vicinity of the antiferromagnetic phase shows the $T^{1.5}$ dependence of resistivity down to low temperature, perhaps due to the strong antiferromagnetic spin fluctuation.

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