論文の内容の要旨

論文題目

Spectroscopic study on charge-spin-orbital coupled phenomena
in Mott-transition oxides

（モット転移酸化物の電荷・スピン・軌道結合物性とスペクトロスコピー）

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Outline

The band theory of solids had been highly successful in describing metals, insulators, and their transitions. The basic distinction between metals and insulators, based on the band structure, was established in the early years of quantum mechanics, and the derived principles well explained many material characteristics including the electronic and optical properties. In 1937, however, several simple transition-metal oxides with a partially filled *d*-electron band were found to be insulators, and then importance of the strong Coulomb repulsion between the electrons was pointed out as a source of the eccentric insulating behavior. In subsequent theoretical approaches, N. F. Mott provided an important foundation of how the electron-electron interactions lead to the insulating phase, and this state is called the Mott insulator. With the strong on-site electron correlation U, the original band would be split into two bands with energy gap of U, and then the system would be an insulator.

One striking point of the Mott insulator is that drastic electronic state changes emerge associated with the insulator-metal (Mott) transition. In the vicinity of the Mott transition, a wide variety of unprecedented phenomena such as high-temperature superconductivity, colossal magnetoresistance, and large thermoelectric effect arises from interplay among charge, spin, and orbital degrees of freedom. While their functional effects may form a significant basis of future oxide electronics, the detailed mechanisms are still under debate. In this thesis, we focus on a couple of transition-metal oxides considered as key counterpart materials to solve the problems, and investigate their charge dynamics and Mott transition features via spectroscopy.

The respective chapters of this thesis are organized as follows. In Chapter 1, an overview is given of the previous key spectroscopic results on Mott-transition oxides. Chapter 2 gives brief descriptions about experimental setups. In Chapter 3, we take $La_{1-x}Sr_xVO_3$ as an typical example of the Mott-transition system and study relationship between the charge dynamics and thermoelectricity. Chapter 4 presents the charge dynamics observed peculiar in a doped valence-bond solid system $(Ti_{1-x}V_x)_2O_3$. In Chapter 5, the charge dynamics and Mott transition features in $R_{2-x}Sr_xNiO_4$ with charge-ordered phases are studied. Finally, we conclude this thesis in Chapter 6, with summarizing the main results. The detailed results of this thesis are as described in the following.

Charge dynamics and thermoelectricity in a typical system (Chap. 3)

A thermoelectric effect finds versatile applications in technologies for energy issues and sustained efforts have been made to explore higher-performance thermoelectric materials. In particular, transition-metal oxides with strong electron correlation have attracted much attention as the promising candidates. One possible important factor for the enhanced thermopower is suggested to be the configurational entropy term as represented in Heikes formula. However, it is still under debate whether the entropy term becomes dominant at merely a few or several hundred kelvin. Although the thermopower in such a correlated electron system should obey the Heikes formula in the high-temperature regimes, the high-temperature crossover behaviors as predicted have not been verified experimentally so far.

In this Chapter, we focus on the vicinity of the filling-control Mott transition, where a metallic state with coherent charge transport realizes only at low temperatures and the thermopower is expected to asymptotically approach the Heikes-formula values with increasing temperature in a manner dependent on the band filling and the Coulomb correlation. Here we adopt the canonical filling-control Mott transition system $La_{1-x}Sr_xVO_3$, where the incoherent charge transport indeed appears above a few hundred kelvin in the Mott critical doping region.

By systematically measuring the high-temperature optical conductivity spectra and thermopower up to 1250 K, we have clarified generic features of how the thermoelectric response is affected by the strong electron correlation. In the vicinity of the Mott transition, the thermopower undergoes two essential crossovers asymptotically approaching the limit values obtained from the Heikes formula. By comparison with results of the dynamical mean field theory for the Hubbard model, we show that the thermopower in the Mott critical state mainly measures the entropy per charge carrier that depends on electronic degrees of freedom available at the measurement temperature. The present findings also offer important clues to the origin of the large thermopower in some correlated oxides; such an idea as focusing on the entropy count of one carrier can be useful for thermoelectric materials design at practical temperatures above room temperature.

Charge dynamics in a doped valence-bond solid system (Chap. 4)

As noted before, the insulator-metal transition has long been one of the central problems in condensed matter physics. In particular, many complex transition-metal oxides with *d*-electrons show the insulator-metal transition, on which the vanishing conductivity is driven either by the divergent carrier mass (sometimes terminated and associated by the onset of the long-range magnetic order) or by the decrease of the carrier density. The electron-correlation driven insulator-metal transition, e.g. in such as V_2O_3 and $La_{1-x}Sr_xTiO_3$, mostly shows the former type, while the insulator-metal transition in high-temperature superconducting cuprates is known to be of the latter type. The electron correlation is the key to the both types of insulator-metal transition, and hence the latter 'doped insulator' like behavior has been argued extensively in terms of novel mechanisms, such as resonating valence bond or pseudo-gap formation. Here we present another

example of the carrier-density driven insulator-metal transition in the *d*-electron system, Ti_2O_3, a classic and most-simple transition-metal oxide but whose detailed charge dynamics (including optical conductivity spectrum) has scarcely been investigated so far.

In this Chapter, we systematically investigate the charge dynamics in thermally and doping induced insulator-metal transitions of $(Ti_{1-x}V_x)_2O_3$ by measuring the optical and transport properties in wide temperature and doping regions. The origin of the observed "doped insulator" like characteristics, such as small Drude weight proportional to the doping level x, is proved to stem from the robust singlet formation on the Ti-Ti dimer. This is in contrast to the prototypical Mott transition in the correlated electron systems, which accompanies the large spectral weight transfer from the Mott gap excitation to the Drude component. The present results probably reveal a novel class of the insulator-metal transition in correlated oxides.

The detailed dynamics of charge carriers in the highly metallic region is also systematically investigated adopting the doped valence bond solid system $(Ti_{1-x}V_x)_2O_3$. We have found that the doped holes show the ferromagnetic correlation and large negative magnetoresistance, while showing an extraordinarily large effective mass (m/m_0~60-80, m_0 being mass of a free electron). We have ascribed such strong mass renormalization to the interaction of doped holes with the dimeric fluctuation or resultant softened phonon on the Ti-dimer sites. The large effective mass seems to conversely favor the strong ferromagnetic correlation. Thus, $(Ti_{1-x}V_x)_2O_3$ can be viewed as a novel magnetic semiconductor, which can be materialized by the strong correlation in the doped valence bond solid state.

Charge dynamics in layered nickelates with charge-ordered phases (Chap. 5)

It is now widely accepted that understanding the nature of a pseudogap is essential for clarifying the whole picture and possible origin of high-T_c superconductivity. Cuprate superconductors behave as an anomalous metal at temperatures above T_c, in which a pseudogap opens with the same momentum-space symmetry as the d-wave superconducting gap. This partially gapped Fermi surface is called 'Fermi arc', which is believed to be a hallmark of the high-T_c superconductors. However, the issue of what kind of order or fluctuation dominates the pseudogap state is still under debate.

A Layered nickelate $R_{2-x}Sr_xNiO_4$ (R: rare earth) has long been known as a counterpart material with typical high-T_c cuprates $La_{2-x}Sr_xCuO_4$; they have common crystal structure and show two-dimensional antiferromagnetic insulator-metal transitions with hole doping procedure. In the metallic state on the verge of the Mott transition, the strong temperature dependence of Hall effect is also common. After several-years' struggle, we could succeed for the first time in growing high-quality single crystals of $R_{2-x}Sr_xNiO_4$ with x exceeding 1.0; this enables us to investigate the detailed electronic structure and charge dynamics in metallic layered nickelates to be compared with those of high-T_c cuprates.

In this Chapter, we investigate the bulk (not surface-specific) nature of the momentum-resolved electronic state for the layered nickelates near the Mott transition for the first time by using the state-of-the-art angle-resolved photoemission spectroscopy with

use of the VUV laser excitation. The metallic but non-superconducting layered nickelate has an x^2-y^2 orbital-derived large hole Fermi surface, which is accompanied with the high-energy pseudogap with the same symmetry and comparable magnitude with those of underdoped cuprates, although its antiferromagnetic interaction J_{AF} is one order of magnitude smaller. Our findings strongly indicate that the high-energy momentum-dependent pseudogap (or Fermi arc) is not unique to the high-T_c cuprates but commonly develops in the anomalous quasi-two-dimensional metallic state near the Mott transition reflecting the real-space checkerboard-type charge correlation.

The pseudogap-related carrier dynamics and critical behavior in the insulator-metal transition is also systematically investigated. In the metallic region proximate to the insulating phase, the carrier number estimated from the Hall coefficient is strongly suppressed accompanied with evolution of the pseudogap structure in the optical conductivity spectra, while the effective mass is relatively small without critical enhancement. Our findings indicate that the checkerboard-type charge correlation dominates the charge dynamics and that the pseudogap evolution induces the insulator-metal transition by gradually vanishing the carrier number in a momentum-dependent form.

Also in this Chapter, the orbital-resolved three-dimensional Fermi surface structure of $Eu_{2-x}Sr_xNiO_4$ is investigated by energy-dependent soft-x-ray angle-resolved photoemission spectroscopy. In addition to a large cylindrical hole Fermi surface analogous to the cuprates, we observe a Gamma-centered $3z^2$-r^2-derived small electron pocket. This finding demonstrates that in the layered nickelate the $3z^2$-r^2 band resides close to the x^2-y^2 one in energy. The resultant multi-band feature with varying orbital character as revealed may strongly work against the emergence of the high-temperature superconductivity.

The multiorbital (x^2-y^2/$3z^2$-r^2) features are important also for understanding electronic structure evolution toward the insulator-metal transition. Doping variation of the hole orbital states is investigated as well, by measuring polarized soft-x-ray absorption spectra. The orbital polarization between x^2-y^2 and $3z^2$-r^2, calculated applying the sum rule to total integrated intensity of the Ni L-edge spectra, increases to nearly zero above x=0.5, which indicates that the excess holes are mainly doped into the $3z^2$-r^2 orbital. Lattice constants a and c show an increase and a decrease above x=0.5, respectively, reflecting the change of the hole orbital states, and the nonmonotonic x variation indicates the strong electron-lattice coupling characteristic of e_g-orbital systems. Numbers of the Ni^{3+} site with occupied $3z^2$-r^2 and x^2-y^2 orbitals, estimated from the preedge peak changes in O K-edge spectra, increase nearly linearly above x=0 and 0.5, respectively. The result is consistent with one deduced from the Ni L-edge spectra, and the both indicate that the checkerboard-type charge/orbital order or correlation strongly persists above x=0.5. The existence of Ni^{4+} sites above x=1.0 may suppress the checkerboard-type ordering and induce the insulator-metal transition at x~1. All these findings well capture the characteristic electronic structure variation toward the metallic region in the layered nickelate.