Electronic structure of SrRuO$_3$

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We have measured photoemission and oxygen $1s$ x-ray absorption spectra of the ferromagnetic metal SrRuO$_3$ and compared them with a first-principles band-structure calculation. The overall distribution of Ru $4d$ and O $2p$ spectral weight is in good agreement with that predicted by the band-structure calculation. However, the observed spectral line shape of the Ru $4d$ band is spread over a wide energy range and the emission intensity at the Fermi level is weakened compared to the band-structure calculation. This implies the importance of electron correlation in the Ru oxide. [S0163-1829(97)05736-6]

Stimulated by the discovery of high T_c copper oxides, much work has been done on various $3d$ transition-metal oxides. In these oxides, electron correlation is important and gives rise to a variety of physical properties. On the other hand, it is generally believed that d electrons in $4d$ transition-metal oxides are less localized and therefore that electron correlation is less important than in the $3d$ oxides. So far, relatively few works have been reported on $4d$ transition-metal oxides and little quantitative information has been obtained about the strength of electron-electron interaction. In fact, Ru oxides exhibit various types of electrical and magnetic properties.[1] For example, rutile-type RuO$_2$ is a normal metal and its density of states (DOS) derived from a band-structure calculation is in good agreement with photoemission spectra.[2] Pyrochlore-type Y$_2$Ru$_2$O$_7$ is an insulator and exhibits a local-moment behavior while Bi$_2$Ru$_2$O$_7$ is a Pauli-paramagnetic metal.[3] Recently, Sr$_2$RuO$_4$ was found to be superconducting below $T_c \sim 1$ K.[4]

In this paper, we present photoemission and x-ray absorption spectroscopic studies of SrRuO$_3$, which is metallic[5] and shows ferromagnetism below $T_c \sim 160$ K.[6–8] We examine the effect of electron correlation by comparing the spectra with first-principles band-structure calculations. SrRuO$_3$ crystallizes in a GdFeO$_3$-type distorted perovskite structure.[9] The saturation magnetization is $1.1–1.3 \mu_B/$Ru[7] and a neutron diffraction study has given $1.4 \pm 0.4 \mu_B/$Ru.[7] According to the ionic picture, the Ru ion is in the tetravalent state and has the electronic configuration of d^4: the Ru^{4+} ion is thought to be in the low-spin ($S=1$) state from the small

magnetic moment. The effective moment of $\sim 2.6 \mu_B$ above T_c is close to the low-spin value of $2\sqrt{S(S+1)} = 2.83 \mu_B$.[6,7] Recently, the magnetotransport properties of SrRuO$_3$ were studied[10] stimulated by the giant magnetoresistance in perovskite-type Mn oxides.[11] In spite of sizable magnetoresistance, it seems that the magnetic and transport properties show relatively independent behaviors.[12,13] Photoemission spectra of SrRuO$_3$ have previously been reported by Cox *et al.*[14] for surfaces heat-treated in an oxygen atmosphere. Recently, Sr$_2$RuO$_4$ has been studied by angle-integrated[15] and angle-resolved photoemission spectroscopy.[16]

Polycrystalline samples of SrRuO$_3$ were prepared by the following procedure: a mixture of RuO$_2$ and SrCO$_3$ was prefired at 800 °C for 12 h in air. Then it was pressed into a pellet and sintered at 1200 °C for 24 h in air. The product was milled and pressed into a pellet again (~ 2000 kg/cm^2). It was then fired at 1300 °C for 24 h in air. X-ray photoemission spectroscopy (XPS) measurements were carried out using a Mg x-ray source ($h\nu = 1253.6$ eV). Ultraviolet photoemission (UPS) measurements were performed using synchrotron radiation (50 eV$< h\nu <$100 eV) at beam line BL-2 of the Synchrotron Radiation Laboratory (SRL), Institute for Solid State Physics, University of Tokyo. The intensities of the spectra taken at different photon energies were normalized to the photon flux determined by the total yield of Au. The total resolution was 0.3–0.4 eV for UPS and ~ 1 eV for XPS. The base pressure in the spectrometers was $\sim 10^{-10}$ Torr. In order to obtain fresh surfaces, we scraped the sample in the ultrahigh vacuum using a diamond file. We

checked the surface condition by monitoring the high binding energy shoulder of the O $1s$ spectrum in XPS or emission at ~ 9 eV below the Fermi level (E_F) in UPS since these features are known due to contamination or surface degradation. In order to avoid quick degradation of the surfaces in ultrahigh vacuum, the samples were cooled to liquid-nitrogen temperature during the scraping and the measurements. Thus the intensity of the high binding energy shoulder of O $1s$ XPS was kept below 30% of the main peak intensity. X-ray absorption (XAS) spectra from the O $1s$ core level were measured at the National Light Source U4B Dragon beamline located at Brookhaven National Laboratory. The energy resolution for the XAS measurements was set at 0.2 eV. The sample was scraped in a dry nitrogen atmosphere and the spectra were recorded at room temperature in the bulk-sensitive fluorescence yield mode.

The DOS of $SrRuO_3$ in the ferromagnetic state has been calculated within the local spin-density approximation (LSDA) using the linearized augmented-plane-wave (LAPW) method. Muffin-tin potential has been used. The result has revealed strong hybridization between the Ru $4d$ and O $2p$ states throughout the whole valence-band and conduction-band regions. The self-consistent result yields a spontaneous magnetic moment of $1.42\mu_B$/Ru, which is lower than that of the low-spin ($t_{2g\uparrow}^3 t_{2g\downarrow} : 2\mu_B$/Ru) configuration of the Ru^{4+} ion. Energy bands primarily of Ru $4d$ character show an exchange splitting of ~ 0.5 eV. The results are in good agreement with recent LSDA calculations by Allen *et al.*[17] and Singh.[18] Spin-orbit interaction in the Ru $4d$ state, which causes the splitting of ~ 0.4 eV in the free atom[19] but is not included in the LSDA calculations, somewhat broadens the Ru $4d$ bandwidth and reduces the DOS at E_F (by $\sim 10\%$).[20]

Figure 1 shows comparison between the measured spectra and the calculated band DOS. Here the UPS spectrum is compared with the total DOS and the XAS spectrum with the oxygen p partial DOS since O $1s$ XAS probes the oxygen p component of unoccupied states. We have convoluted the band DOS with a Gaussian of 0.4 eV FWHM for UPS and XAS and with a Gaussian of 1.2 eV FWHM for XPS. In order to simulate the lifetime broadening effect, convolution with a Lorentzian having an energy dependent width (FWHM$=0.2|E-E_F|$) has been applied. The calculated band structure consists of Ru $4d$-O $2p$ bonding states centered ~ -6 eV, O $2p$ nonbonding states ~ -3 eV, Ru $4d$-O $2p$ antibonding states extending from ~ -2 eV to $\sim +6$ eV, and the Sr $4d$ band centered $\sim +5$ eV. Thus the experimetal features observed between ~ -5 eV and ~ -2 eV are assigned to the Ru $4d$ band and those from ~ -8 eV to ~ -2 eV to the O $2p$-derived band. (The finite emission at -8 to -10 eV would be due to contamination which could not be completely removed by scraping.) First, we notice in the figure that the Ru $4d$ band in the photoemission spectra is considerably broader and the photoemission intensity at E_F is weaker than the band-structure calculation. As mentioned above, spin-orbit interaction broadens the d band only by little and decreases the DOS at E_F only by 10%. In the unoccupied states, on the other hand, the experimental line shape is in relatively good agreement with the
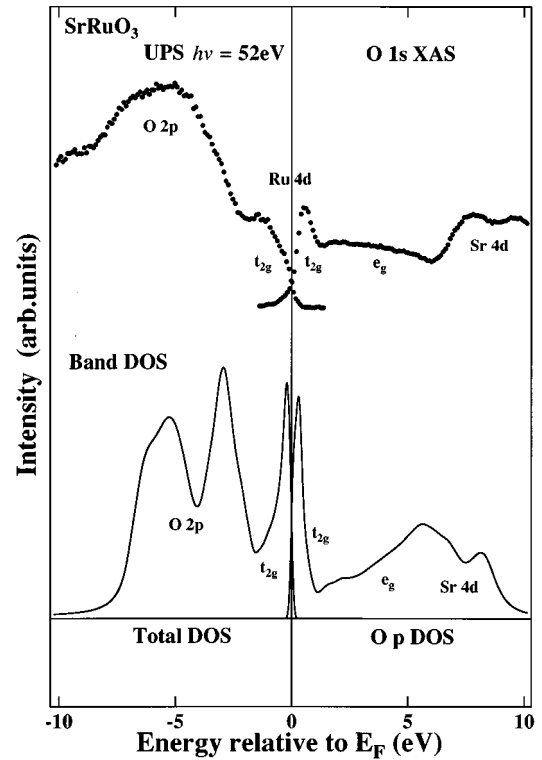

FIG. 1. UPS and O $1s$ XAS spectra of $SrRuO_3$ compared with the band DOS in the ferromagnetic state. The band DOS has been broadened as described in the text. For the XAS spectra, the oxygen p partial DOS is compared.

calculated DOS although the observed intensity at E_F is still suppressed compared to the calculated DOS.

Figure 2 shows Ru $4p$-$4d$ resonant photoemission spectra of $SrRuO_3$. The difference between the on-resonance ($h\nu=52$ eV) and off-resonance ($h\nu=48$ eV) spectra consists of positive contributions from the Ru $4d$ component due to the resonant enhancement and negative contributions from the O
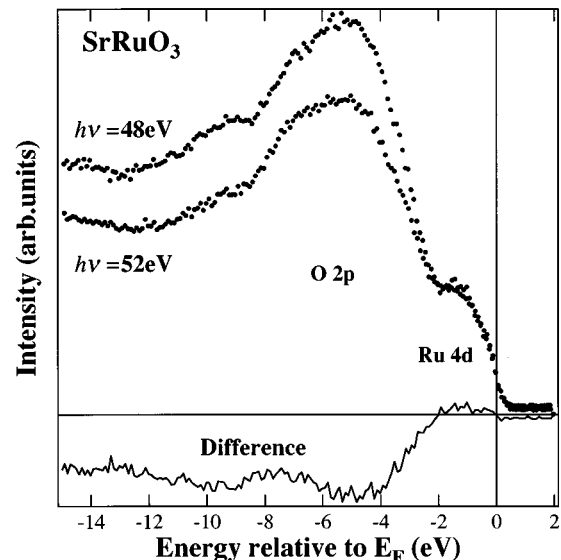

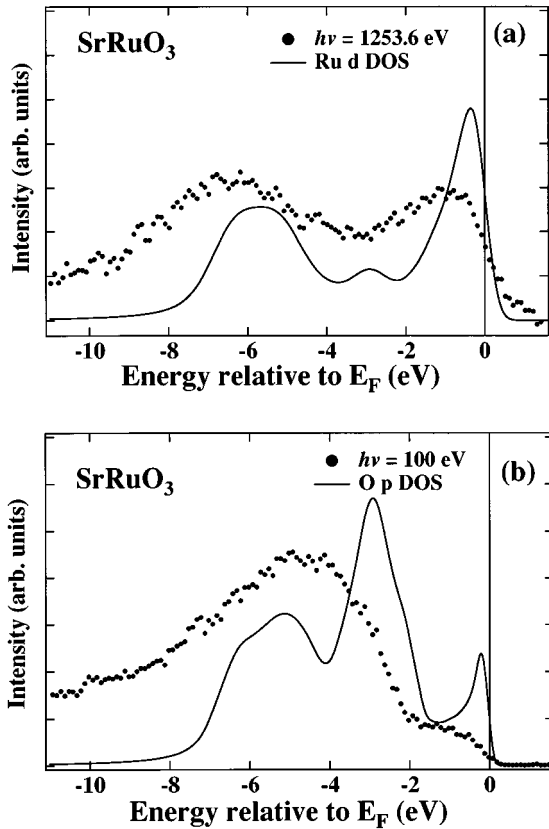FIG. 2. Resonant photoemission spectra of $SrRuO_3$. They are normalized to the photon flux.

FIG. 3. XPS and UPS spectra of $SrRuO_3$. The XPS and UPS spectra are compared, respectively, with the Ru d and oxygen p partial DOS from the band calculation.

$2p$ component due to the decrease of the O $2p$ cross section in going from $h\nu = 48$ eV to $h\nu = 52$ eV. Thus the negative intensity from ~ -2 eV to ~ -10 eV is due to the O $2p$ states and the positive region within ~ 2 eV of E_F has a substantial Ru $4d$ character.

In Fig. 3(a), the XPS spectrum is compared with the Ru d partial DOS derived from the band-structure calculation because the Ru $4d$ cross section is much larger than the O $2p$ cross section for that photon energy.[21] In Fig. 3(b), the UPS spectrum taken with $h\nu = 100$ eV is compared with the oxygen p partial DOS because the Ru $4d$ cross section has a Cooper minimum at $h\nu \sim 100$ eV. Thus we confirm that the band within ~ 2 eV of E_F is mainly of Ru $4d$ character and that at -2 to -10 eV is mainly of O $2p$ character. The peak in the XPS spectrum is located at ~ -6.5 eV, whereas that in the $h\nu = 100$ eV spectrum is located at ~ -5 eV, indicating that the O $2p$ nonbonding band lies above the Ru $4d$-O $2p$ bonding band as predicted by the band-structure calculation.

As pointed out above, the most pronounced discrepancy between theory and experiment is the line shape of the Ru $4d$ band: experiment shows a much broader width and a much lower intensity at E_F than the calculated DOS as shown in Figs. 1 and 3. In addition to the emission near E_F, a broad peak can be identified at ~ 1.2 eV. We tentatively assign the Fermi-edge emission and the 1.2 eV peak to the coherent and incoherent parts of the spectral function, respectively, in analogy with the photoemission spectra of Ti and V oxides[22,23] although the distinction between the two

parts is less clear in the present case.[24] The coherent part represents quasiparticle bands with k dispersions and reflects the itinerancy of the $4d$ electrons whereas the incoherent part represents the remnant of the lower Hubbard band (corresponding to $d^4 \rightarrow d^3$ electron removal spectral weight) and reflects atomically localized excitations. If this assignment is correct, the separation of the incoherent peak from E_F is a portion of the on-site d-d Coulomb interaction U. The incoherent peak in $SrRuO_3$ is shallower than those in the d^1 Ti and V oxides (1.5–1.7 eV below E_F),[22,23,25] indicating that the d-d Coulomb interaction in the Ru oxide is smaller (possibly ~ 3 eV) than that of the Ti and V oxides (~ 4 eV) (Ref. 26) but is still substantial. Here, it should be cautioned that the incoherent part of $SrRuO_3$ may not be a single component as in the d^1 systems but probably contains (broadened) multiplet structures of the d^3 final-state configuration. This is because the photoemission spectra of insulating $Y_2Ru_2O_7$ have shown the d^3 multiplet which is spread over energy range of ~ 2 eV.[14] Even if this was the case, the "coherent part" would be derived from the lowest energy term of the d^3 multiplet, and the phenomenological analysis of the spectral function described below would not be altered. The O $1s$ XAS spectrum does not clearly show incoherent spectral weight (upper Hubbard band) unlike the photoemission spectra.

Now we consider the difference between the band DOS and the photoemission spectra in terms of the self-energy correction $\Sigma(k,\omega)$ to the one-electron band structure ε_k. Here, we ignore the spin dependence of the self-energy for simplicity (which may be justified by the relatively small spin polarization of $SrRuO_3$). The k dependence of the self-energy at E_F reduces the spectral intensity at E_F. The reduction factor is given by

$$\frac{m_k}{m_b} \equiv \frac{\partial \varepsilon_k}{\partial k} \left/ \left[\frac{\partial \varepsilon_k}{\partial k} + \frac{\partial \, \mathrm{Re} \, \Sigma(k,\omega)}{\partial k} \right] \right|_{\omega=0, k=k_F}, \quad (1)$$

where m_k is called "k mass" and m_b is the bare band mass. From Figs. 1 and 3, we estimate $m_k/m_b \sim 0.3$ (taking into account the additional broadening due to the spin-orbit interaction). The relative spectral weight of the coherent part to the total spectral weight is given by

$$\frac{m_\omega}{m_b} \equiv \left[1 - \frac{\partial \, \mathrm{Re} \, \Sigma(k,\omega)}{\partial \omega} \right] \bigg|_{\omega=0, k=k_F}, \quad (2)$$

where m_ω is called "ω mass." Spectral weight $1 - m_b/m_\omega$ absent in the coherent part has been transferred to the incoherent part centered ~ 1.2 eV below E_F. Our data implies that $m_\omega/m_b \sim 10$ although the separation into the coherent and incoherent parts is difficult. The effective mass m^*, which is proportional to the quasiparticles DOS at E_F, is given by $m^* = (m_k/m_b)(m_\omega/m_b)m_b$ (Ref. 23) so that we obtain $m^*/m_b \sim 3$. This value is in reasonable agreement with the mass enhancement factor of 3.7 deduced from the electronic specific heat γ and the band-structure calculation.[17] Not only the enhancement of m^* but also the strong deviation of m_k/m_b and m_ω/m_b from unity indicate that the self-energy correction is substantial and hence that electron-electron interaction is important in $SrRuO_3$. Very

recently, a similar analysis has been made for Sr_2RuO_4, and the same tendency ($m_k/m_b \ll 1$, $m_\omega/m_b \gg 1$ and $m^*/m_b \gtrsim 1$) has been found.[15]

As for the unoccupied states probed by O $1s$ XAS, Fig. 1 shows that the Ru $4d$ band seen in the XAS spectrum and the calculated DOS reasonably agree with each other unlike in the photoemission spectra. In the final state of O $1s$ XAS, in addition to the electron excited into the conduction band, a core hole is created in the O $1s$ level. The latter core hole neutralizes the electric charge of the excited electron in the final state and reduces the many-electron excitations, thus making the spectra resemble the calculated one-electron DOS. Indeed, the O $1s$ XAS spectra of $Sr_{1-x}Ca_xVO_3$ (Ref. 27) are much closer to the DOS given by band-structure calculations than the corresponding x-ray inverse-photoemission spectra,[25] which show coherent and incoherent features. Also, the sensitivity of the O $1s$ XAS to the O $2p$ partial DOS would explain the better agreement for the O $1s$ XAS since the O $2p$ electrons are less strongly correlated than the Ru $4d$ electrons.

In conclusion, electron correlation between the d electrons is significant in $SrRuO_3$ in spite of the relatively extended $4d$ wave functions compared to the $3d$ wave functions in $3d$ transition-metal oxides. The magnitude of the on-site Coulomb interaction U is also found to be sizable. The present spectroscopic results show that electron correlation is important in this system. The photoemission spectra of the superconductor Sr_2RuO_4 exhibit an intense incoherent part and a weak coherent part as in the present system, implying that strong electron correlation is a common feature of a number of Ru oxides.

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