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Evidence for correlation effects in Sr_2RuO_4 from resonant and x-ray photoemission spectroscopy

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We study the electronic structure of Sr_2RuO_4, a noncuprate layered superconductor (T_c=0.93 K), using electron spectroscopy. X-ray photoemission spectroscopy shows that the single particle occupied density of states (DOS) is in fair agreement with the calculated DOS. However, resonant photoemission spectroscopy across the Ru 4*p*-4*d* threshold establishes the existence of a correlation satellite to the Ru 4*d* band. The results indicate substantial charge-transfer character at the Fermi level, with on-site correlations U_{dd} comparable in magnitude to the Ru-O hopping integral, like the cuprates.

Since the discovery of high-temperature superconductivity in oxides,[1] enormous effort has been directed toward making materials which show superconductivity at higher temperature as well as understanding the mechanism of superconductivity. Until now, a large number of cuprate superconductors has come to be known, all of which include CuO_2 plane(s) without exception. Significantly large hybridization between the Cu $3d(x^2-y^2)$ and O $2p\sigma$ states, strong electron-electron correlations on the Cu site, and charge-transfer character of states about the Fermi level (E_F) are generally believed to play an important role for superconductivity.

Recently, it was discovered that Sr_2RuO_4, a noncuprate perovskite layered oxide, exhibits superconductivity at 0.93 K.[2] This material has the same crystal structure as La_2CuO_4 (i.e., K_2NiF_4 structure) with two-dimensional RuO_2 planes instead of the CuO_2 planes. This finding has provoked much attention on how the noncuprate layered superconductor is similar to or different from the cuprate superconductors with much higher T_c's; one may expect that a comparative study gives insight to the importance of CuO_2 planes in high-T_c oxides. In fact, a recent band structure calculation on Sr_2RuO_4 (Ref. 3) predicts that the electronic states at the E_F consist of Ru $4d\varepsilon(xy,yz,zx)$-O $2p\pi$ antibonding bands in contrast to the cuprates, where Cu $3d(x^2\text{-}y^2)$-O $2p\sigma$ antibonding bands cross E_F. While the electronic states at E_F are primarily derived from Ru 4*d* states with a relatively high density of states giving a specific heat γ value of ~10 mJ/K^2mol, this calculated value is still much less than the observed γ value (39–45.5 mJ/K^2 mol).[2,6] Also, the resistivity at temperatures below about 25 K is highly anisotropic (ratio of interlayer to in-plane resistivity is more than 500), but follows a T^2 temperature dependence due to electron–electron scattering for the interlayer as well as the in-plane component.[2,4,5] While La_2CuO_4 is an antiferromagnetic insulator, metallic Sr_2RuO_4 exhibits an enhanced Pauli paramagnetism, implying correlations.[6] Though Sr_2RuO_4 is definitely not as correlated as the cuprates, our results establish that electron correlation effects are necessary to describe Sr_2RuO_4 satisfactorily, as is implied by all transport and thermodynamic measurements.

In this paper, we study the electronic structure of single-crystal Sr_2RuO_4 using x-ray and resonant photoemission spectroscopy. Our results show that the occupied density of states (DOS) consist of primarily Ru 4*d* states at E_F, while the O 2*p* states are centered at about 6 eV below E_F, in overall agreement with the DOS calculated using the linear muffin-tin orbital in the atomic-sphere-approximation (LMTO-ASA) method including matrix element effects. However, resonant photoemission spectroscopy across the Ru 4*p*-4*d* threshold shows the existence of a correlation-induced satellite at about 3 eV binding energy due to a *local two-hole-like final state* in this 4*d* transition metal compound. The electronic structure of Sr_2RuO_4 is understood to exhibit on-site Coulomb correlations, with strong hybridization and substantial charge-transfer character of states at E_F.

Single crystals of Sr_2RuO_4 were prepared by the floating zone method. The details of the preparation will be published elsewhere.[4] The samples were characterized for structure using x-ray diffraction. Magnetic susceptibility measurements confirmed the superconductivity at about 0.9 K. The resonant photoemission measurements were performed using an angle-resolved photoemission spectrometer at the UVSOR synchrotron-radiation center, Institute for Molecular Science, Okazaki. The energy and angular resolutions were 0.3–0.5 eV and 2° for 21–60 eV photon energy. Photoemission measurements were carried out on clean surfaces obtained by *in*

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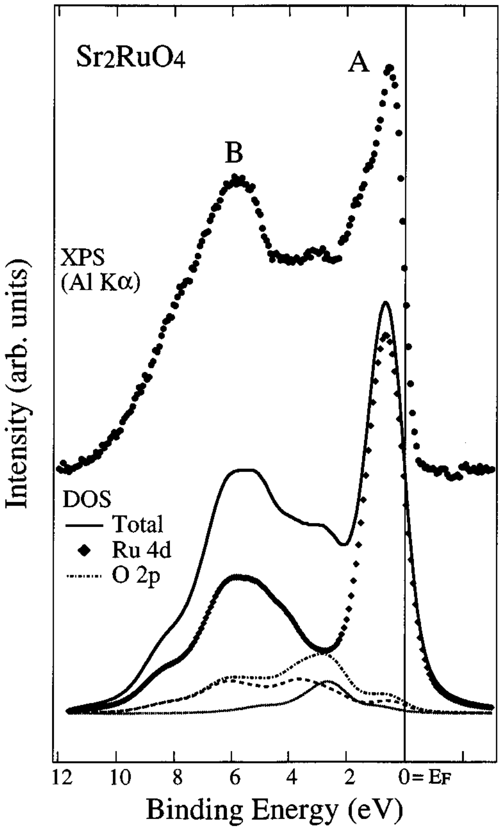

FIG. 1. XPS spectrum of single-crystal Sr_2RuO_4 obtained using Al $K\alpha$ photons (1486.6 eV) at room temperature (upper panel) and the total and partial DOS calculated using the LMTO-ASA method including matrix element effects (lower panel). The total O p partial DOS (dash-dotted line) is further resolved into the p_x, p_y (dashed line), and p_z (dotted line) contributions.

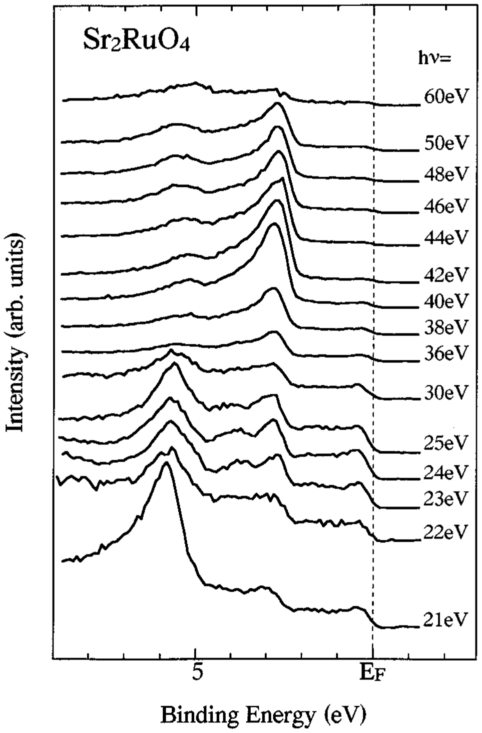

FIG. 2. Valence band photoemission spectra from Sr_2RuO_4(001) obtained using photon energies between 21 and 60 eV at 120 K, showing a clear resonance feature at 3 eV binding energy across the Ru 4p-4d threshold (about 40 eV).

situ cleaving in the analysis chamber. The vacuum was better than 4×10^{-10} Torr and the samples were cleaved and held at a temperature of 120 K throughout the measurements. The spectra showed the formation of the well-known surface contamination and/or degradation derived feature at 10 eV binding energy about 4 h after cleaving. So the spectra presented here were obtained by adding data collected from many samples, measured within 2.5 h of every cleaving. Photoemitted electrons were collected normal to the single-crystal (001) surface. The intensity is normalized to the incident photon flux, and the E_F was referenced to that of a gold film deposited on the sample surface. The x-ray photoemission measurements were performed with a Surface Science Laboratories spectrometer (SSX-100) with a monochromatic Al $K\alpha$ source at a resolution better than 0.8 eV. Samples were cleaved *in situ* at a vacuum of better than 7×10^{-10} Torr. The measurements were done at room temperature with the same care as described above.

Figure 1 shows the x-ray photoemission valence band spectrum of Sr_2RuO_4 obtained using Al $K\alpha$ (1486.6 eV) photons at room temperature. The valence band shows a sharp feature (A) at E_F and a broad feature (B) centered at about 6 eV binding energy. Minor features at about 3 and 8 eV binding energy are also observed. In Fig. 1 we also show the DOS obtained from a self-consistent band structure calculation using the LMTO method in the atomic sphere approximation, incorporating matrix element effects as well as resolution and lifetime broadening.[7] As is clear, the calculated spectrum is in fairly good agreement and reproduces each of the experimentally observed features. To identify the origin of the features, we have also plotted the Ru 4d and O 2p partial DOS in Fig. 1, which basically constitute the total DOS. The peak at E_F consists of antibonding character of the Ru 4$d\varepsilon$ mixed with O 2$p\pi$ derived states, while states of primarily bonding O 2$p\pi$ character mixed with the Ru 4$d\varepsilon$ states occur centered at about 6 eV. The p_x and p_y as well as p_z contributions to the total O 2p derived states are also shown in Fig. 1. The nonbonding states of mostly p_z character in Sr_2RuO_4 lie at about 2–4 eV binding energy. In spite of the above-described fair agreement, there are small differences between the calculated and experimental spectra. For example, the peak at E_F is narrower in the experiment compared to the calculation, possibly due to correlation effects. Also, the spectral shape between 1.5 and 3 eV binding energy is not very well reproduced in the calculation.

In order to further investigate the nature of the states involved in the one-electron removal process, we studied the valence band of Sr_2RuO_4 using resonant photoemission across the Ru 4p-4d threshold. Figure 2 shows the valence band spectra obtained for incident photon energies ranging from 21 to 60 eV. A strong resonance feature is observed across the Ru 4p-4d threshold at a binding energy of nearly 3 eV. In Fig. 3, we plot the integrated area under the resonance feature at 3 eV binding energy compared to that of the feature at E_F. A typical resonance profile at the Ru 4p-4d

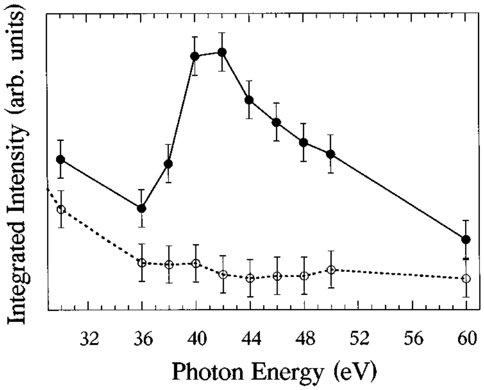

FIG. 3. Integrated area for the resonance feature corresponding to the local two-hole-like final state (between 2 and 4.6 eV binding energy, solid circles) and for the well-screened feature (within 2 eV of the Fermi level, open circles), as a function of photon energy.

threshold is clearly observed for the feature at 3 eV binding energy. Since we performed this experiment using normal emission mode angle-resolved ultraviolet photoemission spectroscopy (ARUPS), we need to eliminate the possibility of this enhancement being an angle-resolved effect. Using a direct transition model and assuming a free electron final state with an inner potential of 10 ± 2 eV (corresponding to the experimental and calculated bottom of the valence band), the change in momentum vector perpendicular to the plane due to change in photon energy from 21 to 60 eV is calculated to be approximately 1.58 ± 0.04 Å^{-1}. On the other hand, for Sr_2RuO_4, the Brillouin zone size between Γ and another high-symmetry point Z perpendicular to the a-b plane is 0.49 Å^{-1}. Thus any change in spectral intensity due to band dispersion perpendicular to the plane should repeat 3 times in the range of measured energies. We clearly do not observe this, and thus the enhancement is not an angle-resolved effect, but a genuine resonance enhancement. Note that while Sr_2RuO_4 has a broad Ru $4p$ core level centered at 46 eV and having a width of more than 8 eV inclusive of the unresolved spin-orbit splitting, its threshold is at about 42 eV. This energy position is almost the same as the peak in resonance absorption (41 eV). The small difference in the binding energy and resonance absorption energy is typical of metal oxides and is due to core-hole effects.[8,11] Having established that the spectral changes are due to a resonance process, it is still surprising because from x-ray photoemission spoectroscopy (XPS) measurements and the band structure calculations (Fig. 1), the primarily Ru $4d$ derived states occur at E_F with a minimum intensity at 3 eV binding energy and no suggestion of a well-defined peak at that energy, in contrast to the experimentally observed spectra shown in Fig. 2. Then the observation that a resonance occurs beyond the $4d$ band at E_F indicates the existence of a correlation-induced satellite to the d band, which alone is resonantly enhanced at the $4p$-$4d$ threshold. This behavior is well known to occur only in strongly correlated electron systems of the $3d$ transition metals, rare earths, and actinides, as well as their compounds,[9] due to the formation of a local two-hole-like final state. For example, the 6-eV satellite in Ni metal[10] resonates due to interference between the direct channel ($d^n+h\nu\rightarrow d^{n-1}+e$) and the photoabsorption channel ($p^6d^n+h\nu\rightarrow p^5d^{n+1}\rightarrow p^6d^{n-1}+e$).

For the case of Sr_2RuO_4, the valence of Ru^{4+} corresponds to a d^4 ground state configuration with possible admixture from the charge-transferred states $d^{4+n}\underline{L}^n$, where $\underline{L}^n$ denotes n holes in the ligand states. Then the one-electron removal spectra shows a resonance due to the local d^3 final state occurring at about 3 eV binding energy, while the well-screened feature at E_F corresponds to the $d^4\underline{L}$ configuration, as the screening channel is via the ruthenium-oxygen overlap. This observation that the local d^3 final state is at a higher binding energy than the $d^4\underline{L}$ state then indicates that Sr_2RuO_4 has substantial charge-transfer character in the ground state. The above observations are very similar to the case of the high-T_c oxides[11] as well as NiO (Ref. 12) and CuO,[8] which have large charge-transfer character. In fact, the well-screened states at E_F corresponding to the $d^4\underline{L}$ configuration show a small resonance dip (Fig. 3), as is also known in the other charge-transfer systems and has been calculated in a cluster model,[13] though it is not very clear here due to the low intensity of the feature at low photon energies.

Since the two-hole-like satellite originates in a quasidiscrete state with two holes localized on the same atomic site, we do not expect separate satellites for the bonding- and antibonding-derived Ru $4d$ states, but only one satellite with a width determined by the multiplet splitting of the final state and its position determined by U_{dd}. One can make a simple estimate of U_{dd} starting from the one-electron band picture. The binding energy of the valence band satellite, due to the localized final states, $[E_0]=2\varepsilon_d+U_{dd}$, where ε_d is the binding energy of the primarily d dervied states. As for ε_d, we referred to the position of the primarly Ru $4d$ band (about 0.6 eV). The resonance satellite is positioned at 2.7 eV binding energy. Thus U_{dd} is estimated to be about 1.5 eV. A similar analysis for the cuprates[11] has shown that U_{dd} is 5–6 eV, while the bandwidth is also about the same value. For Sr_2RuO_4, from a tight-binding fit to the linearized-augmented plane-wave band calculation,[3] the orbital energy difference $E(d\varepsilon)-E[\mathrm{O(I)}p\pi]=1.5$ eV, $E(d\varepsilon)-E[\mathrm{O(II)}p\pi]=0$ eV [where O(I) is an in-plane oxygen atom and O(II) is an oxygen atom perpendicular to the RuO_2 plane) and hopping integrals $pd\pi[d\varepsilon-\mathrm{O(I)}p\pi]=1.5$ eV, $pd\pi[d\varepsilon-\mathrm{O(II)}p\pi]=1.0$ eV, indicating that the ground state of Sr_2RuO_4 has similarities to the high-T_c oxides; i.e., it exhibits on-site Coulomb interactions and substantial charge-transfer character as understood from our spectroscopic results, while the estimated hopping integral is comparable in magnitude to U_{dd}. This photoemission result seems consistent with the specific heat (γ) measurement. While Sr_2RuO_4 exhibits a larger γ value (about 40 mJ/K^2 mol) (Refs. 2,6) than that of $La_{1.8}Sr_{0.2}CuO_4$ (14 mJ/K^2 mol),[14] the ratio of the experimental value to the theoretical one by the band structure calculation[3,15] lies at a similar value of 3–4 in both compounds. However, there are definitely differences in the electronic properties between these two compounds as described above. In order to get a deeper insight to the correlation effect, a comparative photoemission study on other Ru compounds such as $SrRuO_3$, which is a ferromagnetic three-dimensional metal with a smaller γ, is necessary.

In summary, the electronic structure of single-crystal Sr_2RuO_4, a noncuprate layered superconductor, has been studied using x-ray and resonant photoemission spectroscopy. While the XPS results are in fair agreement with band structure calculations, a correlation-induced satellite to the Ru 4*d* band, which exhibits a remarkable resonance across the 4*p*-4*d* threshold, is established. Its origin is ascribed to a localized two-hole-like final state. The study shows that the electronic structure of Sr_2RuO_4 exhibits on-site Coulomb correlations, strong hybridization, and substantial charge-transfer character to states at E_F playing an important role in determining its properties. While the on-site correlation energy is much smaller in Sr_2RuO_4 compared to the cuprates, the U_{dd} is comparable to the Ru-O hopping integral, like the cuprates.

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