Evolution of the Spectral Function in Mott-Hubbard Systems with d^1 Configuration

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We have studied the photoemission spectra of perovskite-type Ti^{3+} and V^{4+} oxides, which have formally the d^1 configuration ranging from a Mott insulator to a paramagnetic metal. The results indicate that as the Mott-Hubbard gap closes, spectral weight is transferred from the upper and lower Hubbard bands to the region near the Fermi level with decreasing U/W (U, d-d Coulomb repulsion energy; W, one-electron d-band width), i.e., from the incoherent to the coherent part of the single-particle spectral function.

Electron correlation in narrow-band systems has been extensively studied using the Hubbard model [1], in which the magnitudes of the on-site Coulomb energy U and the one-electron band width W control the properties of the system: With an integral number of electrons per atomic site, the system is metallic when $U/W < 1$ and becomes insulating when $U/W > 1$. The single-particle spectral function $\rho(\omega)$, i.e., the imaginary part of the single-particle Green's function $G(\omega)$, characterizes physical properties of many-electron systems and can be measured by photoemission and inverse-photoemission spectroscopy. No clear picture for the $\rho(\omega)$ of the Hubbard model, however, has been obtained so far, particularly on the metallic side of the Mott transition. The complication originates from the nature of the splitting between the lower and upper Hubbard bands, which is fundamentally different from the splitting of one-electron energy bands [2].

In this Letter, we have studied the photoemission spectra of various Mott-Hubbard-type $3d$ transition-metal oxides which cover a certain range of U/W values on both sides of the Mott transition. We compare materials with the same d-band filling, namely, Ti^{3+} and V^{4+} compounds having formally the d^1 configuration, since the lowest energy required for the charge fluctuation $d^n + d^n \rightarrow d^{n+1} + d^{n-1}$ ($=U_{eff}$) depends on the multiplet structures of the d^n, d^{n+1}, and d^{n-1} configurations. As a result of the degeneracy of the Ti or V $3d$ (t_{2g}) orbitals, $U_{eff} \sim u' - j$, where u' is the Coulomb energy between two electrons in different t_{2g} orbitals and j is the corresponding exchange integral. Then the Mott transition occurs at $(u' - j)/W \sim 1$, where W is now the width of the t_{2g} band.

We have studied $YTiO_3$ (a ferromagnetic insulator [3]), $LaTiO_3$ (a "barely metallic" antiferromagnet with weak ferromagnetism below $T_C \sim 125$ K [3–5]), and $SrVO_3$ (a paramagnetic metal [6]). They have a cubic ($SrVO_3$) or distorted ($LaTiO_3$, $YTiO_3$) perovskite structure ($GdFeO_3$-type structure); the Ti-O-Ti or V-O-V bond angle is distorted from the ideal value of 180° to $\sim 155°$ in $LaTiO_3$ and $\sim 140°$ in $YTiO_3$ [7]. The distortion reduces the overlap between neighboring d orbitals and hence W in the order $SrVO_3 \rightarrow LaTiO_3 \rightarrow YTiO_3$. In addition, in going from Ti^{3+} to V^{4+} oxides, the metal d level is lowered relative to the oxygen p level due to the increase in the valence and atomic number of the transition-metal ion, which would increase the p-d hybridization and hence increase W and decrease U_{eff}. Thus, U_{eff}/W decreases in the order $YTiO_3 \rightarrow LaTiO_3 \rightarrow SrVO_3$.

Polycrystalline samples were made by a melt-quenching technique, and were characterized by thermogravimetry analysis ($SrVO_{2.99 \pm 0.01}$, $LaTiO_{3.03 \pm 0.01}$, and $YTiO_{3 \pm 0.14}$), x-ray diffraction, dc conductivity, and magnetic susceptibility measurements. Photoemission experiments were performed using a spectrometer equipped with a He discharge lamp ($h\nu = 21.2$ and 40.8 eV) and a Mg x-ray source and also using synchrotron radiation at beamline BL-2 of the Synchrotron Radiation Laboratory (Institute for Solid State Physics, University of Tokyo) and at BL-11D of the Photon Factory (National Laboratory for High Energy Physics). The samples were cleaned *in situ* by scraping with a diamond file. In order to avoid the degradation of the surfaces in an ultrahigh vacuum, the samples were cooled down to ~ 80 K using liquid nitrogen or to ~ 35 K using a closed-cycle He refrigerator during the scraping and data acquisition. The cleanliness of the sample surfaces was checked by the absence of extra features at binding energies 9–12 eV and a high-binding energy feature in the O $1s$ core-level spec-

tra, which arise from contamination or degradation of the sample surfaces. No intrinsic temperature dependence was observed in the spectra although the surfaces were generally very unstable at room temperature.

Figure 1 shows the photoemission spectra of $SrVO_3$ taken with photon energies in the V $3p \rightarrow 3d$ core absorption region. Above the absorption threshold, d-electron emission is enhanced due to the resonance photoemission effect, $3p^6 3d^n + h\nu \rightarrow 3p^5 3d^{n+1} \rightarrow 3p^6 3d^{n-1} + e$. Thus the emission within ~ 3 eV of the Fermi level (E_F) is unambiguously identified with the occupied part of the V $3d$ band. Similarly, the Ti $3d$ origin of the emission within ~ 4 eV of E_F for the Ti compounds has been confirmed [8].

One notices in Fig. 1 that the d band consists of two structures: One is within ~ 1 eV of E_F with a sharp Fermi cutoff and the other is a broad feature centered ~ 1.5 eV below E_F. Figure 2 shows that, in going from $SrVO_3$ to $LaTiO_3$ to $YTiO_3$, the ~ 1.5-eV peak becomes more intense whereas the feature near E_F becomes weaker and finally vanishes in the insulating $YTiO_3$, for which the 1.5-eV feature is unambiguously assigned to the lower Hubbard ($d^1 \rightarrow d^0$) band. That is, the relative intensities of the two features show a systematic dependence on U_{eff}/W. In Fig. 2, we also show the spectrum of another d^1 system, VO_2 [9], whose U_{eff}/W is expected to be smaller than that of $SrVO_3$ because U_{eff} should not be much different among the V^{4+} oxides and W would be larger in VO_2 due to the much shorter V-V distance [10]. Indeed, in VO_2 the high- and low-binding-energy features

are found to be even weaker and stronger, respectively, than those in $SrVO_3$ [11].

In Fig. 2, we compare the spectra with the results of nonmagnetic band-structure calculations. The band structures for $SrVO_3$ and $LaTiO_3$ have been calculated in the local-density approximation using the augmented-plane-wave (APW) method and the localized-spherical-wave (LSW) method, respectively [12], and that for VO_2 is taken from Ref. [13]. The calculated density of states (DOS) has been appropriately broadened to simulate the instrumental and lifetime broadening effects. The emission within ~ 1 eV of E_F corresponds well to the DOS given by the band-structure calculations. We may therefore assign this feature to itinerant d-band states corresponding to the quasiparticle excitations or renormalized d-band states and refer to it as the "coherent part" of the spectral function. The high-energy feature is located at energies close to that of the lower Hubbard band of $YTiO_3$ and has no corresponding feature in the calculated DOS. We therefore attribute this feature to a remnant of the lower Hubbard band and refer to it as the "incoherent part" of the spectral function. In Fig. 2, we also compare the photoemission spectrum of ReO_3 [14] with the band-structure calculation [15]. Because of the extended nature of the Re $5d$ wave functions, $U_{eff}/W \ll 1$, and therefore the photoemission spectrum and the calculated DOS are in reasonable agreement without any sign
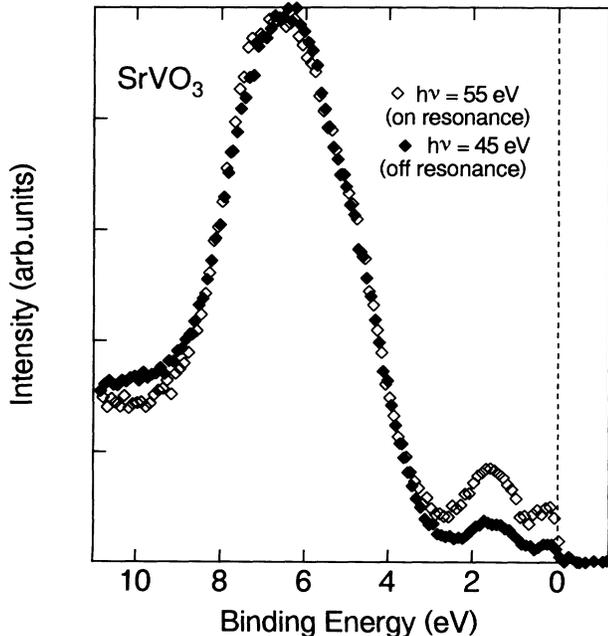
FIG. 1. Photoemission spectra of $SrVO_3$ for photon energies in the V $3p \rightarrow 3d$ core absorption region. The spectra are normalized at the peak of the O $2p$ band.
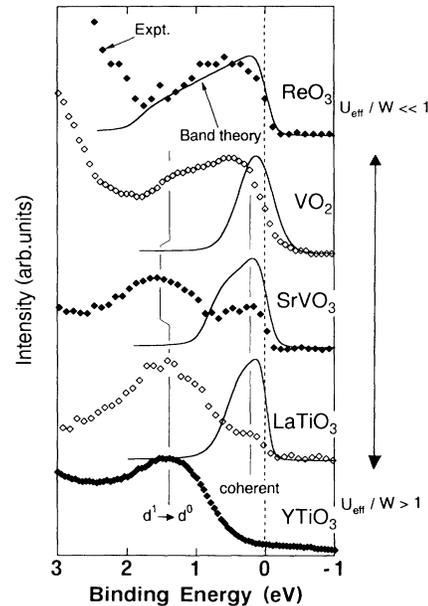
FIG. 2. Photoemission spectra (diamond symbols) of $YTiO_3$ ($h\nu = 21.2$ eV), $LaTiO_3$ ($h\nu = 48$ eV), and $SrVO_3$ ($h\nu = 55$ eV) in the d-band region. The spectra of VO_2 in the metallic phase ($h\nu = 60$ eV) and ReO_3 ($h\nu = 40.8$ eV) are taken from Refs. [9] and [14], respectively. They are compared with the DOS given by band-structure calculations [13,15] (solid curves). The instrumental resolution is ~ 0.5 eV for VO_2 and ~ 0.2-0.3 eV otherwise.

of incoherent spectral weight.

Recently, calculations of the single-particle spectral function have been performed for the single-band Hubbard model at half filling. White et al. [16] have performed a Monte Carlo simulation study of the two-dimensional Hubbard model and shown that with decreasing U/W, the upper and lower Hubbard bands are shifted toward E_F rather rigidly and coalesce into a single band in the $U=0$ limit; the transfer of spectral weight from the incoherent to the coherent part is not very clearly demonstrated. Exact diagonalization studies on small clusters have yielded similar results [17]. Menge and Muller-Hartmann [18] have studied the Hubbard model in infinite dimension in a weak-coupling perturbation theory. Their results show that for $U>0$, the band is narrowed near E_F and that high-energy tails appear, which might correspond to the remnant of the Hubbard bands. Thus the theoretical studies do not necessarily show the persistence of the Hubbard bands in the metallic phase. In order to explain the apparent discrepancy between theory and experiment, effects which have not been taken into account in those theoretical studies, such as the orbital degeneracy of the t_{2g} band, long-range Coulomb interaction, and electron-phonon interaction, might have to be seriously considered.

We shall then analyze the photoemission data phenomenologically by introducing the local self-energy $\Sigma(\omega)$ of quasiparticles, in which electron correlation and other interaction effects are incorporated. The simplest case where the quasiparticle renormalization factor $z(\omega)$ $\equiv [1 - \partial \mathrm{Re}\Sigma(\omega)/\partial\omega]^{-1}$ is constant throughout the t_{2g} band cannot explain the experimental results: With a constant $z(\omega)$ ($\equiv z$), the t_{2g} band would be uniformly narrowed by the factor z and the spectral density at E_F would remain unchanged, leading to the ratio of the coherent spectral weight to the incoherent one of $z/(1-z)$, whereas the photoemission results show that the coherent part is reduced in height rather than in width. The experimental results can be better explained if we allow for the energy dependence of $z(\omega)$ and assume the form of $\mathrm{Re}\Sigma(\omega)$ as shown in Fig. 3, where significant band narrowing [$z(\omega)\ll1$] occurs only in the vicinity of E_F ($|\omega|<\omega_0$) and $z(\omega)$ is of order 1 otherwise. The ω_0 defines the energy scale on which the band narrowing occurs and would decrease with decreasing $z(\omega\sim0)$. As can be seen from Fig. 3, the occupied t_{2g} band width is then reduced roughly by the amount $\sim\omega_0/z(0)$ or by a factor $\sim a \equiv 1 - [\omega_0/z(0)]/W$ and the spectral density near E_F is also reduced by a similar factor. Thus the coherent to incoherent spectral weight ratio becomes $\sim a^2/(1-a^2)$. Using reasonable values $W\sim1$ eV, $1/z(0)\sim10$, and $\omega_0\sim0.01$–0.05 eV, we roughly obtain $a^2/(1-a^2)\sim0.3$–4, and the reduction in the occupied d-band width is only moderate (0.1–0.5 eV), consistent with experiment. Since the spectral density exactly at E_F should remain unchanged by interaction [19], a narrow peak of the width $\sim\omega_0$ is predicted at E_F in the photo-
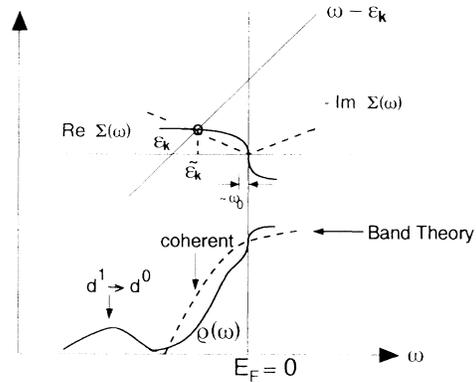
FIG. 3. Proposed energy dependence of the self-energy $\Sigma(\omega)$ and the spectral function $\rho(\omega) \equiv -(1/\pi)\mathrm{Im}G(\omega) = -(1/\pi) \times \mathrm{Im}\{1/[\omega - \varepsilon_k - \Sigma(\omega)]\}$ in the d-band region. The noninteracting electron energy ε_k is shifted by $-\mathrm{Re}\Sigma(\omega)$ to give the quasiparticle energy $\tilde{\varepsilon}_k$. The $\rho(\omega)$ of the noninteracting system (dashed curve) is thus modified to give the measured $\rho(\omega)$ (solid curve).

emission spectra as shown in Fig. 3. The above form of $\Sigma(\omega)$ is, of course, not a unique solution to explain the photoemission data since the present angle-integrated data with moderate energy resolution do not provide very detailed information. In particular, the detailed form of $\Sigma(\omega)$ in the vicinity of E_F should be reflected in low-energy properties such as magnetic susceptibilities and specific heats. High-resolution ($\ll0.1$ eV) photoemission studies at low temperatures will be able to answer these questions to some extent.

If we assume the above form of $\mathrm{Re}\Sigma(\omega)$, Kramers-Kronig relations predict that $\mathrm{Im}\Sigma(\omega)$ significantly deviates from the usual Fermi-liquid behavior, $\sim -\omega^2$, except for the narrow region $|\omega|<\omega_0$ and behaves rather like $\sim -|\omega|$. A limiting case where $\omega_0\rightarrow0$ and $z(0)\rightarrow0$ is referred to as a marginal Fermi liquid [20]. In this case, the interaction is nearly strong enough to make the Fermi liquid unstable and to induce a Mott transition. Indeed, the recent optical study of LaTiO$_3$ ($h\nu>0.1$ eV) [3] has indicated that the effective mass steeply increases toward $h\nu\rightarrow0$ and the relaxation time behaves rather linear in $h\nu$.

In conclusion, we have shown how the coherent part of the single-particle spectral function develops around E_F between the lower and upper Hubbard bands with decreasing U_{eff}/W. We point out that such evolution of the spectral function is apparently similar to that of $4f$ electrons in valence-fluctuating Ce compounds [21] although the underlying model in the latter systems is the impurity Anderson model. The unoccupied part of the spectral functions of the present systems remains to be studied by inverse-photoemission spectroscopy. It is interesting to see how the metallic states produced by the collapse of the Mott-Hubbard gap resemble or differ from those produced by carrier doping [2] and how the situation changes in going from the Mott-Hubbard regime to the

charge-transfer regime. It is also important to obtain a unified picture for the single-particle and two-particle spectral functions, which can be probed by (inverse) photoemission and optical absorption, respectively, because the coherent spectral weight appears considerably enhanced in the latter compared to the former spectral function [22].

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