Spin-resolved photoemission of valence-band satellites of Ni

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(Received 30 September 1996; revised manuscript received 30 October 1996)

Spin-resolved photoemission spectra of 6-, 9-, and 13-eV satellites of the ferromagnetic Ni valence band are reported. The spin polarization of the valence-band satellites and their photon energy dependence are interpreted by the multiplet configuration of $3d^8$ and $3d^7$ final states. This implies the localization of a photoexcited final state reflecting the strong electron correlation in Ni. [S0163-1829(97)04211-2]

I. INTRODUCTION

Core-level and valence-band photoemission spectra of strongly correlated electron systems often show satellite structures in addition to the main spectral features. One of the main reasons for the great interest in the satellites is that the analyses of binding energies and spectral profiles give important information on the electron-correlation effects, where a photoexcited hole plays a crucial role as a test charge and a test spin in the electron system.

So far, the electronic structure of ferromagnetic Ni has been the subject of intensive studies for many years.[1–15] In Ni, $3d$ electrons are strongly correlated and the effective Coulomb interaction between $3d$ electrons is of the same magnitude as twice that of the bandwidth.[4] In the valence band spectra of Ni, electron correlation effects appear as a reduction of the valence bandwidth compared with that expected by a one-electron approximation and satellites which are observed up to 30 eV below the Fermi level.[1–3] In the valence-band satellites, most work has dealt with the 6-eV satellite, which corresponds to a two-hole bound state localized at a Ni atom and reveals a resonant enhancement at the $3p$ threshold.[5–12] The origin of the enhancement of the 6-eV satellite near the $3p$ threshold is now understood as being due to the interference between two photoelectron excitation processes; one is the direct $3d$ valence-electron excitation ($3p^6 3d^9 + h\upsilon \rightarrow 3p^6 3d^8 + \mathrm{el}$) and the other is the $3p$ core electron excitation followed by the $M_{2,3}VV$ super Coster-Kronig transition forming the two $3d$ holes in a same atomic site ($3pp^6 3d^9 + h\upsilon \rightarrow 3p^5 3d^{10} \rightarrow 3p^6 3d^8 + \mathrm{el}$).

If we assume on the basis of a simple atomic model that a $3d$ hole exists in the minority-spin states of a ferromagnetic Ni, the spin polarization of the 6-eV satellite was expected to take its maximum value at the $3p$ threshold.[8] Experimentally, it was found that the spin polarization of the 6-eV satellite takes its maximum value at the $3p$ threshold, in a good agreement with the theoretical expectation.[9] This observation was crucial evidence against alternative explanations for the origin of the resonance enhancement of the 6-eV satellite such that as due to the interband transition from s,p-like valence bands.[10]

In this paper, we present the spin-resolved photoemission of the valence-band satellites of a ferromagnetic Ni(110) single crystal including the so-called 6-, 9-, and 13-eV satellites. We investigate their spin polarization in connection with the origin of the satellites.

II. EXPERIMENT

The spin-resolved photoemission experiments were carried out at the Revolver undulator beamline BL-19A of the Photon Factory, which is equipped with an angle-resolved photoelectron spectrometer and a 100-keV Mott detector for the photoelectron-spin analysis. A Ni(110) single crystal was shaped into a picture frame with each side to orient along the easy magnetization axis of $\langle 111 \rangle$ and was remanently magnetized during the measurements. A clean Ni(110) surface was obtained by repeated cycles of ion bombardment and annealing. The cleanliness of the sample surface was checked by low-energy electron diffraction and Auger electron spectroscopy. The photoelectrons emitted normal to the sample surface were collected with the angle of incident light of 20°. The energy resolution of the observed spin- and angle-resolved photoemission spectra was about 0.4 eV at an excitation energy of 65 eV. A more detailed description of the experimental procedures was presented elsewhere.[11]

III. RESULTS AND DISCUSSION

Figure 1 shows majority- and minority-spin spectra of ferromagnetic Ni at an excitation energy below the $3p$ threshold (67 eV). The photoelectron intensity of the majority-spin satellite is larger than that of the minority-spin satellite, which causes the positive spin polarization of the 6-eV satellite.[13] The spin polarization is shown in Fig. 1(b). In the majority-spin spectrum a broad feature with weak peaks at 6.4 and 5.5 eV is observed, while a broad feature has a weak peak at 5.6 eV in the minority-spin spectrum. If we assume in a simple atomic model that the spin momentum is conserved during

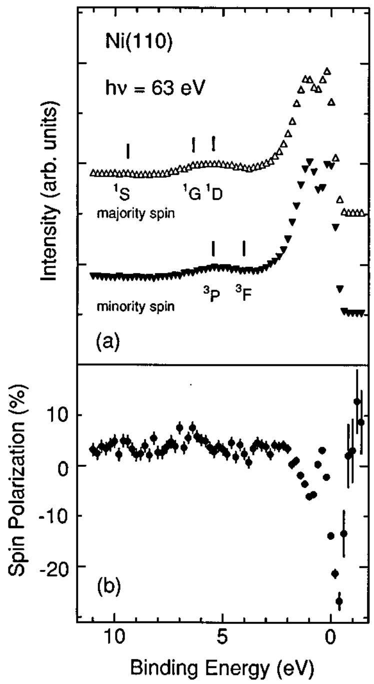

FIG. 1. (a) Majority- and minority-spin spectra of Ni(110) observed at an excitation energy of 63 eV. Vertical bars correspond to the position of the $3d^8$ final-state configuration expected by an atomic model. (b) Spin polarization of the Ni valence band. The statistical error is indicated by bars in the figure.

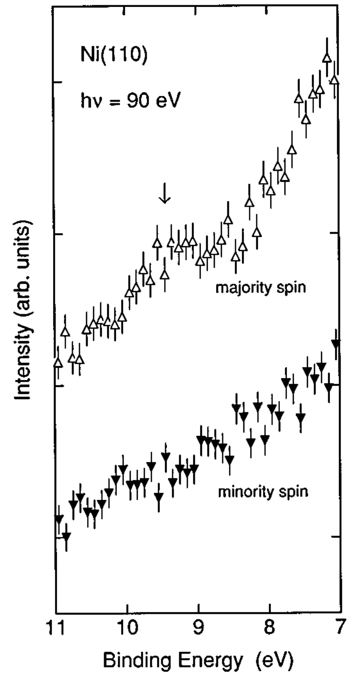

FIG. 2. Majority- and minority-spin spectra observed at an excitation energy of 90 eV. The calculated position of the $^1S3d^8$ final state is indicated by an arrow. The statistical error is indicated by bars in the figure.

the photoemission process, the minority-spin spectrum only consists of the spin triplet $3d^8$ final states, whereas both spin singlet and triplet final $3d^8$ states contribute to the majority-spin spectrum.[16] Vertical bars with symbols indicate the positions of the $3d^8$ final states expected by a simple atomic model best fitted to the observed spectral features.[17] To calculate the term splitting energies, we adopted the Racah parameters as $B=0.10$ and $C=0.45$ eV. The intense peak at 6.4 eV in the majority-spin satellite corresponds to the $^1G3d^8$ final state which dominantly contributes to the positive spin polarization of the 6-eV satellite.[13] The weak peaks around 5.5 eV both in majority- and minority-spin spectra correspond to the $^1D3d^8$ and $^3P3d^8$ final states, respectively.

In the atomic model, a spectral feature corresponding to $^1S3d^8$ final state is to be observed at the binding energy around 9 eV with a 100% spin polarization. However, the spectral feature of the 9-eV satellite is not clearly observed in the majority-spin spectrum of Fig. 1 due to its small intensity, but the spin polarization reveals a hump at the binding energy near 9 eV. Figure 2 shows the majority- and minority-spin spectra obtained at excitation energy of 90 eV in an expanded scale. In the figure, we could observe the weak spectral feature at 9.4 eV only in the majority-spin spectrum in agreement with the atomic model. The excitation energy of 90 eV was chosen not only to maximize the photoelectron intensity to improve the accuracy of the spectrum but also to avoid the superposition of $M_{2,3}VV$ Auger electrons on the valence-band satellites. Since the normal-emission spectrum of Ni(110) corresponds to the band dispersion along the Γ-K-X direction of the Brillouin zone, spectral features that originated from the s-like Σ_1 band are expected to be observed around 9 eV in both majority- and minority-spin spectra at an excitation energy of 90 eV.[18] However, at the small angle of incident light (20°), the vector potential parallel to the sample surface predominantly contributes to the photoelectron excitation and the normal-emission spectra of Ni(110) mainly consists of Σ_4 bands.[19] In addition, at an excitation energy of 90 eV the contribution of the s-like Σ_1 band would be suppressed due to the small ionization cross section compared with the d-like Σ_1 band near the Fermi level. The s-like Σ_1 band has not been observed even in spin-integrated spectra.[20] Hence the feature at 9.4 eV that we observed in the majority-spin spectra corresponds to the $^1S3d^8$ final state. The large spin polarization of the ^1S satellite is also consistent with the theoretical expectations.[21,22] In the above analysis, we have neglected the possible contribution of the $^4F3d^7$ final state, since its intensity is expected to be very small. Thus, the spectral profiles of the 6- and 9-eV satellites in the Ni valence band are likely to be interpreted by a simple atomic model due to the strong localization of the photoproduced valence hole. Our results support the recently observed spin-resolved photoemission spectra of valence-band and core-level satellites of Ni, where a large intra-atomic electrostatic interaction between valence electrons and photoproduced hole as well as inter-atomic hybridization cause the satellite structures.[13–15]

Recently, Tanaka and Jo[23] calculated the spectral profile of the valence-band satellites of Ni from the viewpoint of the configuration interaction using the impurity Anderson model adopting atomic multiplets. In the model, the itinerant character of Ni $3d$ electrons is not treated explicitly but is adopted as the hybridization between $3d$ states and other valence states. They reproduced not only the resonant enhancement of the 6-eV satellite near the $3p$ threshold but the photon energy dependence of the spin polarization of the

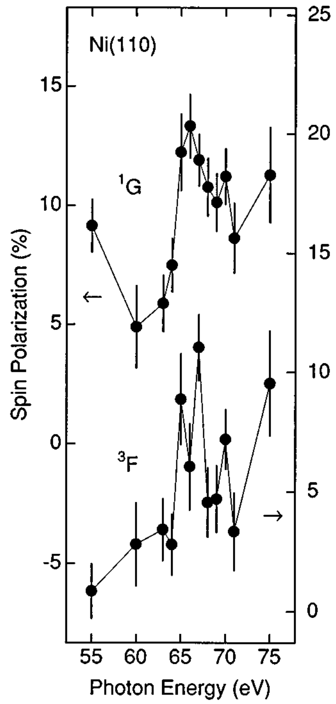

FIG. 3. Photon energy dependence of the spin polarization of the spectral features at the binding energy of 6.4 and 3.8 eV, which corresponds to ^1G and ^3F terms in the final state, respectively. The thin lines connecting experimental results are drawn to separate the photon energy dependences of ^1G and ^3F terms for the sake of clarity and are not intended to show peak and dip structures explicitly.

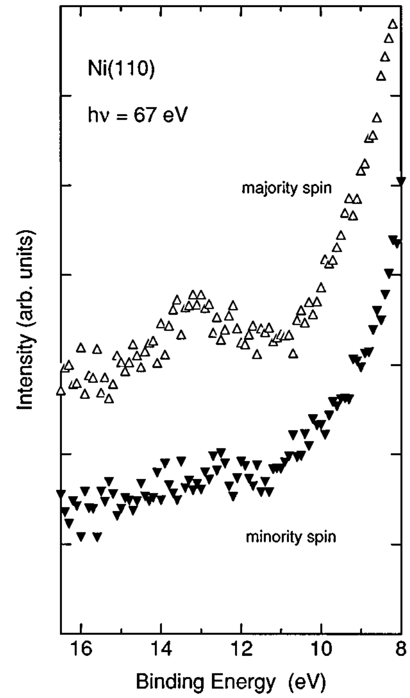

FIG. 4. Majority- and minority-spin spectra of the 13-eV satellite observed at the 3p threshold.

6-eV satellite, which shows a dip structure near the 3p threshold.[11,12] According to their calculation, the dip profile is mainly due to the photon energy dependence of the ^1G term which predominantly contributes to the 3d^8 final state with a positive spin polarization and does not necessarily manifest a Fano profile near the 3p threshold. The spin polarization of other terms may show different photon energy dependence, e.g., ^3F term reveals a negative spin polarization and a maximum around the 3p threshold.

In Fig. 3, we show the photon energy dependence of the spin polarization of a different part of the 6-eV satellite. Although each term of the 3d^8 final state may consist of many multiplets due to the multipole 3d-3d and 3d-3p interactions, we represent the ^1G and ^3F terms as the spectral features at the binding energies of 6.4 and 3.8 eV, respectively, which are expected by a simple atomic model. In spite of the fact that the observed spin polarization includes large statistical errors, it is obvious from the figure that the spin polarization of ^1G and ^3F terms show different photon energy dependences. In the figure, ^1G term shows a larger spin polarization than the ^3F term as expected by the atomic model and ^1G term shows a dip profile below the 3p threshold, whereas ^3F term shows rather a peak near the 3p threshold. This qualitatively manifests the different photon energy dependences between ^1G and ^3F terms expected by the calculation.[23]

Recently, it was claimed that the resonant enhancement of the 6-eV satellite at the 3p threshold could be described completely by a superposition of incoherent $M_{2,3}VV$ Auger electrons due to the strong delocalization of the photoexcited intermediate state.[24] Our results indicate that the photon energy dependence of the 6-eV satellite could be comparatively well explained by the model adopting atomic multiplets where the photoexcited state is localized at a Ni atom and the resonance enhancement of the 6-eV satellite is described as an interference between two photoexcitation processes. The calculation based on the same model could also reproduce the angular dependence of the 6-eV satellite of a polycrystalline Ni near the 3p threshold.[25]

It has been observed that a weak valence-band satellite exists around 13 eV below the Fermi level.[26,27] The photoelectron intensity of the 13-eV satellite reveals a sharp resonance enhancement at the 3p threshold and a broad maximum at a slightly larger photon energy (74 eV). In the atomic model, the satellite consists of doublet and quartet 3d^7 final states and ^2G and ^4P terms manifest at the binding energy around 13 eV.[28] The photon energy dependence implies the strong localization of the photoexcited 3p core hole intermediate state which leads to the 3d^7 final states. In the present experiments, the photoelectron intensity of the 13-eV satellite was so small that the 13-eV satellite was only observable at the 3p threshold and not around 74 eV where the broad hump was observed in the previous spin-integrated experiments. Figure 4 shows the majority- and minority-spin spectra of the 13-eV satellite region observed at an excitation energy of 67 eV. In the figure, the spectral intensity of the majority-spin state is much larger than that of the minority-spin spectrum. This implies that the spin polarization of the 13-eV satellite is enhanced at the 3p threshold. By subtracting smooth backgrounds from majority- and minority-spin spectra, the net spin polarization of the 13-eV satellite was found to take a maximum value of 52$\pm$15% at the spectral feature of 13.2 eV.

IV. CONCLUSION

In conclusion, the spectral profiles of the spin-resolved photoemission spectra of 6-, 9-, and 13-eV satellites of a Ni valence band can be interpreted by the atomic multiplets of the $3d^7$ and $3d^8$ final states. This applicability of the localized model to the photoexcited state is maintained by the strong electron correlation in Ni.

ACKNOWLEDGMENTS

The authors are pleased to thank Professor H. Fukutani, Professor T. Jo, Professor J. Igarashi, Professor Y. Sakisaka, and Dr. A. Tanaka for stimulating discussions.

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