New Observation of the Valence-Band Satellite in Ni(110)

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The valence-band photoemission of Ni(110) shows that the two-hole satellite appears at a constant binding energy of 6.0 eV away from the $3p \rightarrow 3d$ resonance in accord with earlier results, but on resonance it shifts to ~6.8 eV. Interpretation of this new result in terms of the singlet and triplet satellite states is proposed.

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Recently, a valence-band satellite in Ni photoemission, which is enhanced near the $3p \rightarrow 3d$ resonance,[1] has been a subject of high interest for experimental[2-4] and theoretical studies.[5-8] The origin of the satellite is rather well understood and is ascribed to the two-d-hole bound state. This satellite has been reported to have an onset at ~25-eV photon energy ($h\nu$) and appears then at a constant binding energy of ~6 eV for higher photon energies.[1,2] This Letter reports observation of the shift in the position of the satellite for Ni(110) near the $3p$ resonance which has not been reported previously. The s-band emission, which should not be confused with the satellite, is not expected to be enhanced for $h\nu$ at the $3p$ resonance in normal emission from Ni(110), in contrast to the case of Ni(100) or Ni(111) where the final electron-energy band approaches the Brillouin-zone boundary at X or L near the $3p$ resonance.

The clean Ni(110) surface was prepared by repeated cycles of Ar^+-ion sputtering and annealing. The amounts of impurities were reduced to less than the detection limit of Auger spectroscopy (e.g., the Auger-peak height ratio, O(KLL, 510 eV)/Ni(LVV, 848 eV), was less than $\frac{1}{400}$ and this corresponds to a coverage of 0.003 monolayer or less). The photoemission measurements were carried out at Photon Factory, National Laboratory for High Energy Physics, using a 150° spherical-sector-type analyzer with an acceptance of ±1° and a PHI 15-255G double-pass cylindrical-mirror analyzer (CMA).[9] Total experimental resolution varied from 0.3 eV for $h\nu=24$ eV to 2 eV for $h\nu=120$ eV. Throughout the whole set of experiments, the component of the vector potential (**A**) of the light which is parallel to the sample surface was in the $[1\bar{1}0]$ direction ($A_\parallel$ along $[1\bar{1}0]$). Data were normalized to the relative flux of incident photons. The base pressure in the system was 1×10^{-10} Torr.

Figure 1 shows angle-integrated photoelectron spectra of clean Ni(110) measured with the CMA for $25 \leq h\nu \leq 120$ eV. Binding energy is referred to the Fermi energy (E_F). Two structures at ~0.5 and 1.5 eV are attributed to emissions from the $3d$-like bands. For $h\nu > 69$ eV the ordinary (incoherent) $M_{23}VV$ super-Coster-Kronig (sCK) emission is observed. This is seen as broad peaks marked by arrows. The sCK emission appears at the binding energy $E_B = h\nu - 60$ eV, i.e., at a fixed kinetic energy of 60 eV as referenced to E_F. For reference, the expected peak position of the sCK line is indicated by arrows for the 66–68-eV spectra also, where the sCK emission is not prominent. The feature at ~6 eV observed for $h\nu > 30$ eV is the widely studied valence-band satellite. In accord with earlier results[1-3] the satellite is enhanced near the $3p$ threshold ($h\nu_{thr}$ =66–67 eV). However, it should be noted that this peak moves with $h\nu$. The binding energy of the satellite takes the constant value of 6.0 eV for $30 \lesssim h\nu \lesssim 65$ eV (below resonance) and $h\nu \gtrsim 75$ eV (above resonance), but shifts to ~6.8 eV at $67 \lesssim h\nu \lesssim 70$ eV (on resonance).

The above results obtained with the CMA, that the satellite appears at 6.0 eV off resonance and at ~6.8 eV on resonance, were confirmed by five sets of normal-emission photoemission measurements. Figures 2 and 3 show examples of normal-emission spectra of clean Ni(110) taken at the angles of light incidence of $\theta_I = 25°$ (predominant $A_\parallel$ and small $A_\perp$ components, parallel and perpendicular to the surface) and 60° (both $A_\parallel$ and $A_\perp$), respectively ($A_\parallel$ along $[1\bar{1}0]$). Therefore, in prin-

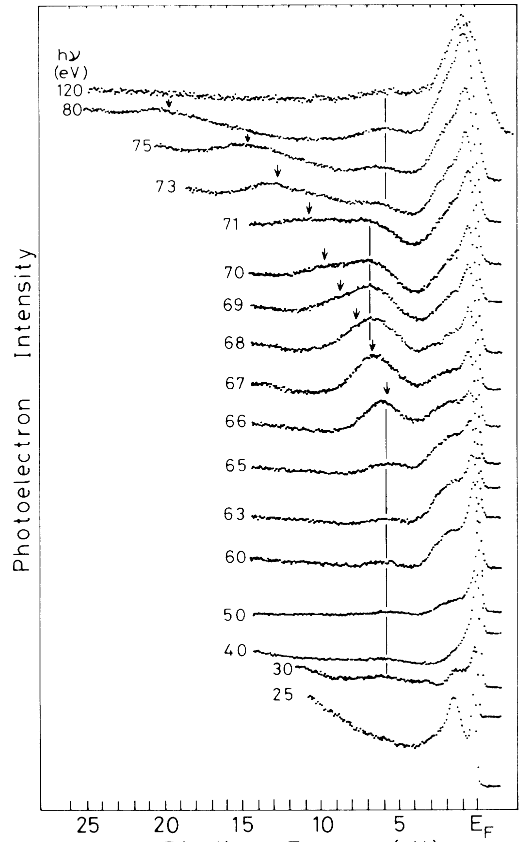

FIG. 1. Angle-integrated photoelectron spectra of a clean Ni(110) surface measured at $25 \leq h\nu \leq 120$ eV. The arrows indicate the expected peak position of the $M_{23}VV$ sCK line. The solid lines are only intended as an aid to the eye and represent the positions of the satellite off resonance and on resonance determined from two sets of angle-integrated measurements.

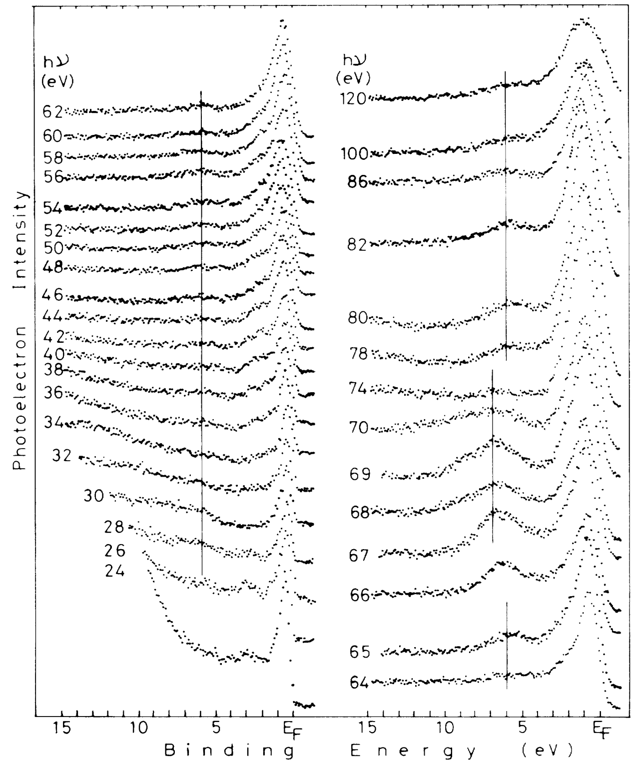

FIG. 2. Normal-emission photoelectron spectra of clean Ni(110) measured at $\theta_l = 25°$ ($A_\parallel$ along $[1\bar{1}0]$) as a function of $h\nu$. The solid lines represent the positions of the satellite off resonance and on resonance determined from five sets of normal-emission measurements.

ciple we can observe primarily the Σ_4 symmetry bands in Fig. 2 and both the Σ_1 and Σ_4 bands in Fig. 3. From comparison of the spectra in Figs. 2 and 3, we can distinguish between the Σ_1- and Σ_4-band emission peaks. For example, the peaks observed at ~0.5 and 2.9 eV for $h\nu = 24$ eV are ascribed to the d-like Σ_4 and Σ_1 bands, respectively. If we assume a free-electron final band with an inner potential, $V_0 = 10$ eV, for the case of Ni(110) which was determined by fitting the free-electron parabola to the calculated final bands with Σ_1 symmetry obtained by Szmulowicz and Pease,[10] we can map the binding energies of all the peaks onto points along the Γ-K-X direction in the bulk Brillouin zone. All the experimental points plotted over the calculated band structure[11] of ferromagnetic Ni along the Γ-K-X direction are shown in Fig. 4 (open circles). For convenience, the position of the 6–7-eV feature obtained by two sets of angle-integrated photoemission measurements (e.g., Fig. 1) is also plotted on the same figure (crosses). The resulting experimental dispersions as well as locations of the bands agree with the bands calculated by Weling and Callaway,[11] except for the fetaure at 6–7 eV. The 6–7-eV feature is not ascribed to the emission from the O2p-derived states (see Ref. 9) or the s-like Σ_1 bands but to the satellite, because the sample surface is very clean as stated above and this feature is observed in similar intensity both for $\theta_l = 25°$ and for $\theta_l = 60°$ in contrast to the peak at 2–3 eV due to the same Σ_1-symmetry bands.

Figure 5 shows the $h\nu$ dependence of the heights of the 0.5-eV peak (normal-emission data, triangles; CMA data, crosses), the 6–7-eV satellite (normal-emission data, empty circles; CMA data, plusses), and the sCK peak (normal-emission data, squares; CMA data, filled circles), observed for the clean surface. The constant-final-state spectrum with a final-state energy of 10 eV and emission normal from Ni(110) is also shown. The curve for the 0.5-eV peak observed by the CMA shows a typical antiresonance dip near the 3p threshold as reported previously,[3] whereas the curve for the 0.5-eV peak observed in normal emission shows a very small or no dip

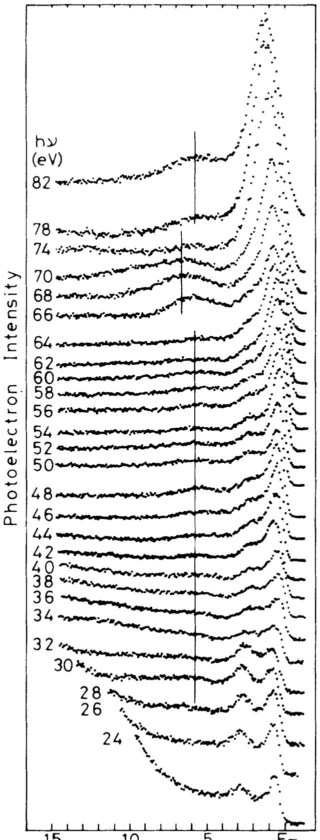

FIG. 3. Same as in Fig. 2 except that θ_l is now 60°.

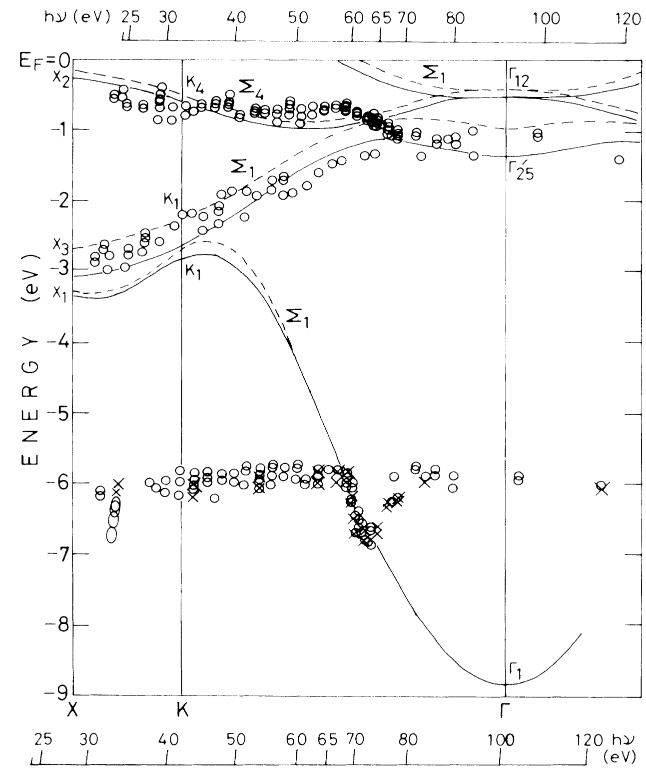

FIG. 4. Portions of the band structure of ferromagnetic Ni along the Γ-K-X direction in the bulk Brillouin zone. The binding energies of the peaks obtained by normal-emission measurements are represented by open circles. The solid and dashed curves denote the majority (↑)- and minority (↓)-spin bands with Σ_1 and Σ_4 symmetries calculated by Weling and Callaway (from Ref. 11). For convenience, the position of the 6–7-eV feature obtained by angle-integrated measurements is also plotted (crosses).

and resembles the constant-final-state spectrum. The satellite peak has its maximum intensity slightly above the $3p$ threshold in accord with the earlier results.[1-3] This enhancement of the satellite near the $3p$ resonance ($67 \lesssim h\nu \lesssim 70$ eV) where it appears at ~6.8 eV is believed to be due not to the overlap of incoherent sCK Auger emission (it is very weak for $h\nu < 70$ eV) but to the coherent Auger decay following the $3p \rightarrow 3d$ photoexcitation (see Fig. 6 of Ref. 8). Our computer work showed that the simple overlap of the Auger emission failed to reproduce the satellite shift ($\lesssim 0.1$ eV compared to ~1 eV observed).[12]

The movement of the satellite from 6.0 eV off resonance to ~6.8 eV on resonance cannot be explained completely by the existing theories.[5-8] It was suggested[6-8] that for the single-band, strongly ferromagnetic Hubbard model (a filled ↑ band and a partially filled ↓ band) only photoemission from the ↑ band has a satellite state (singlet) which is viewed as a hole in the ↓ band bound to a hole in the ↑ band on the same site (the d^8 configuration). When orbital degeneracy is included, the satellite is expected to occur for photoemission from both spin bands: the triplet satellite for ↓-band emission and the singlet and triplet satellites for ↑-band emission. The energy of the singlet satellite is thought to be larger than the triplet one by the exchange integral J (~1 eV) or more (also see Ref. 7). The recent spin-polarized photoemission measurement[4] on Ni(110) showed that the singlet satellite state (the $d^8\,{}^1G$ multiplet in atomic notation) is dominant on resonance in accord with the prediction by Feldkamp and Davis.[6] However, the $h\nu$ dependence of the singlet-satellite to triplet-satellite intensity ratio is not clear at present. If the triplet-satellite state (e.g., ${}^3f$) is important off resonance and the singlet-satellite state (e.g., ${}^1G$) is dominant on resonance, the present results can be rationalized. Along this line, we can try to estimate the expected shift in the satellite peak on resonance versus off resonance by calculating the mean energy of the peak. The principal multiplets of the d^8 configuration are ${}^1G$ and ${}^3F$ separated by 2.6–2.8

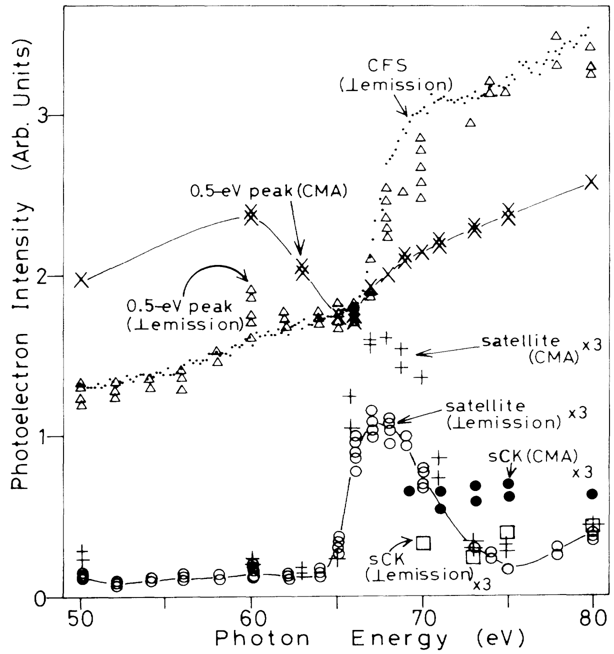

FIG. 5. $h\nu$ dependence of the heights of the 0.5-eV peak, the 6–7-eV satellite peak, and the sCK emission for the clean Ni(110) (see text). The constant-final-state spectrum is also shown.

eV.[13] According to Ref. 6, the ratio of $\uparrow$ to $\downarrow$ emission is $\sim$4.0 on resonance. Singlet peaks contribute only to $\uparrow$ emission while triplet peaks contribute 2/3 to $\downarrow$ emission and 1/3 to $\uparrow$ emission. If we assume that the $\uparrow$-to-$\downarrow$ emission ratio is small off resonance, say 5:4 ($d_\uparrow^5 d_\downarrow^4$ for the ground state), the shift is estimated to be $\sim$1 eV in rough agreement with experiment.

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