PHYSICAL REVIEW B VOLUME 52, NUMBER 15 15 OCTOBER 1995-I

Resonant valence-band satellite in NiGa

Li-Shing Hsu*
Department of Physics, National Chang-Hua University of Education, Chang-Hua, Taiwan, Republic of China

(Received 28 November 1994)

Valence-band photoemission spectra of NiGa were measured with synchrotoron radiation at photon energies around the Ni 3*p* core excitation threshold. The valence-band satellite in NiGa is resonantly enhanced, and it has about the same Fano parameter and effective Coulomb interaction as those for elemental Ni. These observations suggest that the Ni *d* band in NiGa is not completely filled. The number of holes per Ni atom in the Ni *d* band for NiGa is estimated to be 0.33. The effective Coulomb interaction between two 3*d* holes on the same site is 4.6 eV off resonance and 5.3 eV on resonance.

Resonant photoemission (RP) is understood as an atomic process as described by Fano[1] to explain line shapes in core absorption edges. RP's at the 3*p* and 2*p* excitation thresholds of Ni metal were discovered by Guillot *et al.*[2] and by Wu *et al.*,[3] respectively. The phenomenon consists of a resonancelike increase of a photoemission peak located about 6 eV below the Fermi energy (E_F) when the photon energy ($h\nu$) is varied in the vicinity of the Ni 3*p* or 2*p* absorption threshold. In the case of the Ni 3*p* resonance, the resonant enhancement of the valence-band (VB) satellite is caused by the interference of two excitation channels leading to the same final state. The interaction between the discrete channel ($3p^63d^94s \rightarrow 3p^53d^{10}4s$) and the continuum channel ($3p^63d^94s \rightarrow 3p^63d^84s\varepsilon l$) coupled via the super-Coster-Kronig (sCK) decay ($3p^53d^{10}4s \rightarrow 3p^63d^84s\varepsilon l$) gives rise to a Fano-type line shape. A large amount of the theoretical and experimental work of RP from transition metals and their compounds has been reviewed by Davis.[4]

The existence of the VB satellite in Ni is related to the fact that Ni has a partially filled *d* band, which allows the creation of a two-hole bound state on some Ni atoms after a photoionization event.[5] A similar but weaker resonance is also observed in Cu,[6] Zn,[7] Ga,[8] and Pd (Ref. 9) metals. However, for 3*d* transition metals lighter than Ni, such as Cr,[10–12] Mn,[13] Fe,[10,14–16] and Co,[10] the existence of the resonant VB satellite is quite controversial. It has been shown that the number of 3*d* holes (or 4*s*-4*p* holes if the 3*d* band is full) is important in determining the strength of the RP in transition metals.[17] In compounds, the strength of the resonant enhancement of the VB satellite is related to the overlap of the *p* core-hole and *d* valence states. Thus, RP can be used to probe the transition-metal *d* character and hybridization, and is a particularly useful technique for studying the electronic structure of the transition-metal compounds.[18,19] Many studies have characterized the photon energy dependence of the Ni satellite feature in compounds such as $NiCl_2$,[20] $NiBr_2$,[21] NiO,[22–24] NiS,[24] NiTe,[22] NiSb,[22] NiAs,[25] Ni_xSi,[26] and Ni_xCu_{1-x} alloys.[27] In the compounds studied to date, Ni has been the less electronegative species.[28] Thus the occupation of the *d* states should be less than in elemental Ni. In the cases studied, the VB satellite was still present and exhibited resonant behavior very similar to that for Ni metal. The electronegativity values of the partner elements for some Ni compounds are listed in the first column in Table I. We note that there are several electronegativity scales in the literature, in which the most widely cited in many textbooks is that of Paulings.[29] Sacher and Currie[30] pointed out that except for the Pauling electronegativities, there is general agreement among various scales. The differences between these and the Pauling values (with the Pauling values usually higher), particularly among the transition series, were shown to be due to nonlinear problems with the thermodynamic approach on which the latter are based. There is little reason to choose among them, although the Gordy-Thomas scale[28] is used in Table I.

Here we present a RP study of NiGa, a compound in which there should be some electron transfer to Ni atoms from the less electronegative Ga, and thus a higher occupation of the *d* states. It should be noted here that an approximate linear relationship is found between the work function and electronegativity of metals.[28,31] The work functions for Ni and Ga are 5.2 and 4.0, respectively, implying that Ga is less electronegative than Ni, which contradicts many wrongly cited textbook electronegativity values for Ga. To our knowledge, there are no band-structure calculations and inverse-photoemission studies

TABLE I. Electronegativity, I_{sat}, and n_h values for Ni and Ni compounds.

	Electronegativity[a]	I_{sat} (%)[b]	n_h[c]
Ni	1.8	100[d] (67;63)	0.50
NiCu	2.0	55[e] (67;60)	0.35
NiAs	2.0	51[f] (68;64)	0.34
NiGa	1.5	49[g] (67;60)	0.33
NiTe	2.1	39[h] (66;63)	0.28
NiSb	1.8	24[i] (66;64)	0.19
NiS	2.5	7[j] (66;64)	0.07

[a] Electronegativities of the partner elements, Ref. 28.
[b] Resonant satellite intensity. The numbers in parentheses are the on-resonance and off-resonance photon energies (in eV) for calculating I_{sat} values. See text for explanation.
[c] The number of holes per Ni atom in the *d* band.
[d] From Ref. 8.
[e] From Ref. 27, Fig. 2.
[f] From Ref. 25, Fig. 1.
[g] This study.
[h] From Ref. 22, Fig. 4(a).
[i] From Ref. 22, Fig. 5(a).
[j] From Ref. 24, Fig. 10.

reported on NiGa. Thus RP offers an alternative to answer the question of *d*-band filling in NiGa. The intent of this study was to see what effect a decrease in the hole concentration of the Ni *d* band would have on the photoemission satellite and its resonant behavior.

Preparation of the polycrystalline NiGa sample was reported in a recent paper.[32] Since NiGa has rather large disorder parameter,[33] it is expected that the NiGa sample used in this study may contain some defects. Nevertheless, powder x-ray diffractometry showed that it was a single phase and of CsCl structure.[34] Experiments were carried out on beam line VIII-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). Photon energies were selected with a toroidal grating monochromator (TGM), and a PHI 15-255G double-pass cylindrical mirror analyzer (CMA) was used in the constant-pass-energy mode to collect the photoelectron spectra. To increase the counting rate, the energy resolution of the photoemission spectra was set to 0.5 eV at an excitation energy of 30 eV, and to 0.8 eV at 160 eV by adjusting the TGM slit full open and the CMA pass energy to 50 eV. The pressure during the measurements was 8×10^{-9} Torr. A mass spectrum showed that residual gases inside the chamber at this pressure value are hydrogen, methane, water, carbon monoxide, and carbon dioxide. The mass-to-charge ratio of O_2^+ (32) is absent in the mass spectrum, which means that oxygen contamination on the sample surface comes from other molecules containing oxygen. The NiGa surface was cleaned by repeated cycles of argon-ion bombardment and annealed to 350 °C for 15 min. It was reported that contamination or conversion of the Cu(100) surface was a problem at a pressure of low 10^{-9}-Torr range as noticeable changes in low-energy electron-diffraction patterns and ultraviolet photoemission spectroscopy spectra were observed within 1–2 h.[35] Therefore, results reported here involved less than 2 h of collection time before the sample was recleaned. The sample surface from which RP data were obtained contained about 3% of a ML of O and 6% of a ML of C, as estimated from an Auger spectrum[34] collected with the CMA. The sample surface after ion bombardment and annealing contains about 10% more Ni atoms than those in the bulk as determined from the peak ratio of Ni (848 eV) to Ga (1070 eV) *LMM* Auger transitions. It is worthwhile noting that these Auger electrons come from roughly 15 Å from the top of the NiGa surface, while photoelectrons for photon energy between 60 and 80 eV come from about 5 Å in depth. The surface composition within the photoelectron emission depth at $h\nu=40$ and 80 eV is, however, richer in Ga by 49% and 43%, respectively, as determined from the Ni 3*d* and Ga 3*d* peak areas and theoretical photoionization cross sections.[36] This is not surprising, since adsorption of CO or H significantly attenuates the transition-metal *d* bands.[37] A study of the electronic structures of nine Ni-Ga and Ni-In intermetallic compounds[38] using x-ray photoemission spectroscopy (XPS) showed that all of them (except Ni_3Ga_2) are richer in Ni within the XPS sampling depth (roughly 20 Å) after Ar^+-ion bombardment and subsequent annealing. In that study, the NiGa surface, which has a combined oxygen and carbon contamination of less than 1 at. %, is richer in Ni by 16% as confirmed by both XPS and Auger spectra. Thus the NiGa surface within the photoelectron emission depth of this study is most likely Ni rich by about 10%. The preferential sputtering of the gallium atoms from the NiGa surface agrees with that observed for the oxygen deficiency after Ar^+-ion bombardment for the NiO surface.[39]

Figure 1(a) shows the energy distribution curves (EDC's) for NiGa for 60 eV $\le h\nu \le$ 80 eV. The binding energy (E_B) is referred to E_F, and all the spectra are normalized to equal intensity at the maximum of the Ni 3*d*-band emission, which consisted of only one peak at $E_B=0.8$ eV. The determination of E_F for NiGa has been published elsewhere.[38] The satellite at ~6 eV below the Ni 3*d* peak is enhanced near the 3*p* threshold ($h\nu=67$ eV). It is well known that chemisorption of oxygen on Ni causes a strong decrease in the number of *d* holes,[40] and should also weaken the intensity of the resonant satellite. Therefore, a set of spectra similar to that in Fig. 1(a) was taken, and is shown in Fig. 1(b) in order to see the effect of oxygen contamination to the resonant satellite intensity. These spectra have O and C contaminations of 19% and 6% of a ML, respectively, as estimated from Auger intensity of each element. This corresponds to about 1.6 L (1 L=1 Langmuir=10^{-6} Torr s) of oxygen exposure.[14] We notice that at this oxygen coverage, the room-temperature oxidation of Ni is well below the onset (10-L oxygen exposure) of nuclear and lateral growth of NiO islands.[41] We also note that the resonance from the O 2*p* states in single-crystal TiO_2 or Ti_2O_3 is reported to be very strong,[19] while the resonance behavior of the O 2*p* emission from oxidized Ti single crystals[42] does not

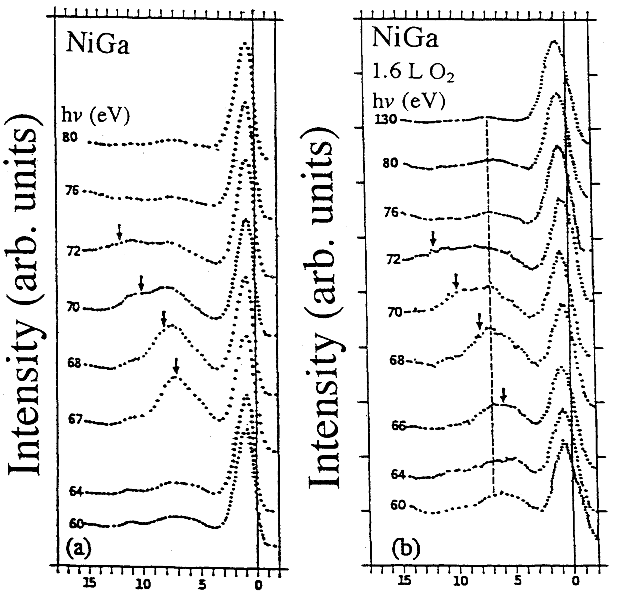

FIG. 1. Photoemission spectra of (a) NiGa and (b) NiGa with 1.6 L oxygen on the surface. The dashed line in (b) indicates the location of the peak of the oxygen-derived emission. Arrows indicate the locations of the $M_{2,3}VV$ sCK emission. Excitation energy is indicated at each curve. All the spectra are normalized to equal intensity at the maximum of the Ni 3*d*-band emission.

show the dramatic resonance seen in titanium-oxide compounds. This is due to the relatively small amount of TiO_2 formed in the oxidation process (1.5-L O_2) on the Ti surface. Since Ni or Ga is more inert than Ti, we assert that, even at 1.6-L oxygen exposure, the NiGa surface is, for the worst case, covered by a very small amount of chemisorbed oxygen. The oxygen coverage on the NiGa surface is so small that it does not affect the strong enhancement of the satellite at resonance, as shown in Fig. 1(a). The dashed line in Fig. 1(b) represents the peak position of the O $2p$ band emission at $E_B=7$ eV. The peak positions of the $M_{2,3}VV$ sCK emission, which are observed for $h\nu \geq 67$ eV, are marked by arrows in Figs. 1(a) and 1(b). As for the water contamination problem on the NiGa surface, we notice that on certain faces of Ni at room temperature, H_2O dissociates, and sometimes adsorbs, only in the presence of preadsorbed oxygen.[43] Since the fingerprint peaks of the OH^- radical[44] at $E_B=4.7$ and 8.0 eV are absent in the photoemission spectrum at $h\nu=40$ eV for NiGa,[45] there is either no or very small amount of adsorbed oxygen on the NiGa surface.

It is very likely that the oxygen detected by Auger comes from chemisorbed CO, since no detectable O_2^+ signal was observed in a mass spectrum taken just before the photoemission experiments. In fact, at $h\nu=30$, 40, and 50 eV, two features with peak binding energies of 7.8, 7.6, and 7.6 eV and 10.6, 11.2, and 11.2 eV, respectively, were observed.[45] We attribute the higher- and lower-binding-energy features to emission from the CO 4σ and CO $5\sigma/1\pi$ orbitals, respectively, due to chemisorbed CO on the NiGa surface. These binding-energy values are close to those reported for CO chemisorption on Ni(100), Ni(110), and Ni(111) surfaces,[46] and on the NiAl(110) surface[47] at 300 K. The CO 4σ level stays at around $E_B=11$ eV up to $h\nu=90$ eV as can be seen clearly from the spectra in Fig. 1(a). Above $h\nu=90$ eV, it disappears almost completely. The CO $5\sigma/1\pi$ level is hidden by the strong resonance of the 6-eV satellite for 60 eV$\leq h\nu \leq$80 eV, and further hidden by the sCK transition above $h\nu=68$ eV. In order to separate the CO $5\sigma/1\pi$ level and the 6-eV satellite, a narrower optical slit opening than used throughout this study was utilized, and two peaks with binding energies of 6.2 and 7.4 eV were resolved at $h\nu=60$ eV. We assign the higher- and lower-binding-energy peaks to the CO $5\sigma/1\pi$ level and the 6-eV satellite, respectively. Shinn and Madey[48] have argued that if the symmetry of the 4σ orbital of α_1 CO (lying down on the surface) is not changed by bonding to the Cr(110) surface, the 4σ peak intensity should be less than that of the combined $(5\sigma+1\pi)$ feature. Since the CO exposure in this study (estimated to be about 0.5 L) is below the onset exposure (1 L) for the appearance of the 4σ orbital of α_2 CO (terminally bonded configuration) on Cr(110),[48] only the lying-down configuration is observed and the α_1 CO $4\sigma:(5\sigma+1\pi)$ intensity ratio for NiGa is indeed less than unity. Greuter *et al.*[49] reported that for a concentration of H below $\sim$0.5 of a saturated coverage on Ni(111), which is likely the case in our study, the H-Ni split-off state merges into the bulk bands, making it a resonant state which is very difficult to observe. We thus point out that the value of the resonant satellite intensity for NiGa reported in Table I may have a larger uncertainty than those for other nickel compounds due to H or CO adsorption.

To obtain an absolute value of the intensity of each peak as a function of $h\nu$, the intensity of the incident light was measured for each spectrum of NiGa. The intensities of the Ni $3d$ and satellite peaks, which were measured at the peak maxima to avoid the problem of background subtraction, are then normalized to the incident photon intensity. Figure 2 shows the corrected intensities of the Ni $3d$ and satellite peaks for NiGa as a function of $h\nu$. The dashed and solid lines in Fig. 2 are to enhance the visibility of the changes in the intensity. The Ni $3d$ excitation spectrum shows interference dips at 67 and 72 eV, and the satellite shows a strong resonance near 69 eV. The antiresonance dip in the d-band intensity was observed in many transition metals [Cr,[10] Ni,[23,50–52] and Cu (Ref. 53)] and their compounds [CuO,[53] Cu_2O,[53] NiO,[23] MnSi,[54] FeSi,[54] CoSi,[54] Ni_xSi,[26] and GaP (Ref. 8)] and explained theoretically[17] by the resonance between the direct excitation from the d band and the threshold excitation from the $3p$ core level. The separation of the double dips in the d-band intensity in the vicinity of the Ni $3p_{3/2}$ and $3p_{1/2}$ core excitation thresholds in 5 eV, a value almost three times the spin-orbit splitting of the Ni $3p_{3/2}$ and $3p_{1/2}$ levels.[55] Thus we do not attribute the double-dip structure to the spin-orbit splitting of the Ni $3p$ levels. In any case, the dip for NiGa is much deeper than that for the copper oxide[53] or the nickel silicide[26] system. The sharp maximum in the excitation spectrum of the Ni $3d$ band at 70 eV might be due to the overlap with states that are responsible for the huge resonance of the satellite peak near 69 eV, since it has the maximum at roughly the same photon energy. The maximum in the Ni $3d$ resonance emission occurs at essentially the same photon energy in both Ni (Ref. 50) ($h\nu=71$ eV) and NiGa ($h\nu=70$ eV), which can be inter-

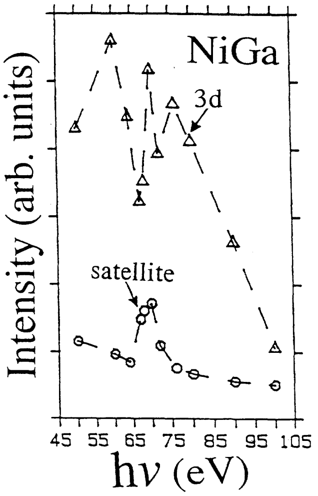

FIG. 2. Intensity of $3d$ and satellite structures in the photoemission spectra of NiGa normalized to the incident photon energy. The curve labeled $3d$ (Δ) represents the heights of the $3d$-band emission peak as a function of photon energy. The curve labeled satellite (O) represents those of the satellite. The dashed and solid lines are to guide the eyes.

preted, following Bertel, Stochbauer, and Madey,[42] as evidence of a significant degree of localization of the Ni $3d$ resonance. The resonance is stronger in the satellite than in the d band for NiGa, a phenomenon also observed in nickel chloride.[20] The resonance-antiresonance feature of the satellite is asymmetric, which is similar to that for Ni.[2,17,50,52] We note that the resonant behavior of the satellite in Cu is nearly symmetric as a Lorentzian,[6] and the absorption is from the $3p$ to the $4s$-$4p$ band ($3d^{10}4s$ initial-state configuration). This observation indicates that the initial state in the RP process is NiGa is largely a partially filled d state ($3d^8 4s^2$ and $3d^9 4s$ configurations), and configuration mixing between these two initial states contributes significantly to the 6-eV satellite. The sp state may participate but is not dominant.[17] This assertion was also confirmed by XPS study of NiGa.[32,38] The strong Ni $3d$-band resonance for NiGa is then due to the $3d^8 4s$ final state ($3d^9 4s$ initial state), which is the same configuration for the Ni metal $3d$-band resonance.[22] It should be pointed out here that although some d spectral weight is present at E_F for NiGa, the clearest and surest signature of empty d bands in NiGa is the 6-eV satellite peak and its resonant behavior, since determination of E_F for NiGa involves some uncertainty as large as 0.2 eV,[38] which is caused by the limited instrumental resolution. We also note that there is no satellite feature observed for the Ga $3d$ peak ($E_B = 18.5$ eV) in this and previous studies[32,38] of NiGa, and the corrected intensity versus $h\nu$ plot for the Ga $3d$ peak[45] does not show as large a variation as that of the Ni $3d$ peak in Fig. 2. Thus weak hybridization is expected between Ga $3d$ and Ni $3d$ orbitals in NiGa. This is not unreasonable, considering the large energy difference (roughly 16 eV) between these orbitals. More quantitative explorations of the d-band filling in NiGa are given in the following.

The excitation spectrum for the 6-eV satellite can be analyzed using the Fano function

$$F(\varepsilon) = (q+\varepsilon)^2/(\varepsilon^2+1) \ , \tag{1}$$

$$\varepsilon = (h\nu - h\nu_0)/\Gamma \ . \tag{2}$$

Here $h\nu_0$ is the resonance energy, Γ is a quantity like the self-energy of the resonance, ε is the normalized excitation energy, and q is an asymmetry parameter in Fano's theory. The parameter q is determined roughly by the optical transition-matrix element relative to the sCK matrix element. As a crude estimation, q can also be obtained from the following relations:

$$q = \gamma + (\gamma^2+1)^{1/2} \ , \tag{3}$$

$$\gamma = h\nu_p / h\nu_h \ . \tag{4}$$

Here $h\nu_p$ is the separation between the locations of the minimum and maximum of the excitation spectrum, and $h\nu_h$ is the half-height width. The q value for the satellite structure of NiGa thus obtained is about 2.4, which is close to the corresponding value ($q = 2.5$) for Ni(100) reported by Guillot *et al.*[2] The satellite peak for NiGa has its maximum intensity at 69 eV, which is slightly above the Ni $3p$ threshold in accord with the earlier results for Ni.[2,6,50,52] Their difference (about 2 eV for NiGa), which is a function of q, is expected to be small; however, without a well-defined Fano line shape in the experimentally derived profiles, quantifying this difference is difficult. The maximum and minimum in the Fano profile can be obtained from Eqs. (1) and (2) as $h\nu_0 + \Gamma/q$ and $h\nu_0 - q\Gamma$, respectively. From these two extreme values ($h\nu = 69$ and 64 eV) of the experimentally derived Fano profile, we obtained Γ and $h\nu_0$ values of 1.8 and 68 eV, respectively, for NiGa, which are close to the corresponding values for Ni (Ref. 2) ($\Gamma = 2.0$ eV, $h\nu_0 = 66$ eV). The difference between the peak value of the Fano profile and $h\nu_0$ is about 1 eV for NiGa, which is close to that for Ni obtained experimentally[2] (0.8 eV) or theoretically[17] (0.7 eV). As pointed out by Guillot *et al.*,[2] the values of Γ and $h\nu_0$ for Ni are in excellent agreement with those of the theoretical calculation,[56] and the q value for Ni is considerably larger than those obtained from either energy-loss spectra[56,57] ($q = 0.9$ and 1.3) or theoretical calculation[56] ($q = 1.8$). We also note that Kakizaki *et al.*,[58] studying the $h\nu$ dependence of the spin polarization of the 6-eV satellite of Ni(110) at various temperatures, found that $q = 0.6$ and $h\nu_0 = 64.5$ eV independent of sample temperature. Equations (1) and (2) predict that, for a small-q value, the height of the resonantly enhanced peak is small compared with the depth of the antiresonance dip. This corresponds to a relatively high value of the product of the sCK matrix element and the transition matrix element for the direct $3d$ emission relative to the matrix element for the $3p \rightarrow 3d$ transition. One thing worth noting is that the dip profile of the 1-eV peak for the clean Fe(110) sample suggests a small-q value, and no satellite feature was found in Fe.[14] All these observations mean that different final states can have different resonant behaviors, and thus different q values.[59] The small difference in the q values for Ni and NiGa is then an indication that the resonant satellites for both materials correspond to a two-hole bound state ($3d^8 4s$ final-state configuration). Thus the Ni d band in NiGa is not completely filled.

In order to compare our data with those of Miyahara *et al.*,[27] we define the resonant satellite intensity I_{sat} the same way as was done by them. Briefly, it is defined as the area of the resonant satellite structure above the background curve normalized by the spectral intensity of the Ni $3d$ band which is defined by the area of the Ni $3d$ band component above the background. For simplicity, we chose a linear background. The resonant satellite structure is obtained by taking the difference between the spectra of on resonance and off resonance. This procedure eliminates the possibility of oxygen $2p$ contribution, if any, to the resonant intensity. The I_{sat} values thus calculated for Ni and Ni compounds are listed in the second column of Table I. The on-resonance and off-resonance photon energies for Ni and Ni compounds are enclosed in parentheses and separated by colons following the I_{sat} values in Table I. According to an XPS study of the electronic structures of nine Ni-Ga and Ni-In intermetallic compounds,[38] a faster filling of the Ni d bands for a Ni concentration less than 50% in these compounds is supported by the fact that I_{sat} values decrease more slowly from Ni to NiGa or NiIn than from 1:1 compounds to $\mathrm{Ni_2Ga_3}$ or $\mathrm{Ni_2In_3}$. However, the complete filling of the Ni d band is not supported, since a sharp decrease in I_{sat} value and a complete disappearance of the 6-eV satellite are not observed in these two series of compounds. If the Ni *d* band is completely filled in NiGa, the final state of the $3p \rightarrow nl$ excitation is either a 4*sp* state or an unoccupied state with partial *d* character (due to *s*-*d* hybridization). In either case, the I_{sat} value for NiGa should be much less than that for Ni. This is the case for NiS and NiSb, but not for NiGa. This is the second indication that the Ni *d* band in NiGa is not completely filled.

It is well known that the important interactions which determine the presence of a satellite, its intensity, and position are the 3*d*-band-width (W), the core-hole–3*d*-electron Coulomb attraction energy (Q), and the band filling.[60] The experimental occupied *d*-band-width for Ni, which is defined as the energy separation between the L_1 points and E_F, is 3.3 eV.[61] The *d*-band-width for NiAl, defined as the energy difference between R_{12} and $R_{25'}$, is 2.6 ± 0.25 eV (Ref. 62) as measured by use of angle-resolved photoemission. The density-of-states-type XPS *d*-band-width, with uncertainties introduced by the lifetime and instrumental broadenings, for NiGa, is 3.2-eV full width at half maximum (FWHM),[38] while that measured in this study is 1.8-eV FWHM with ±0.2-eV variation in the photon energy used. It clearly shows that the *d*-band-width measured with angle-integrated photoemission is a strong function of resolution. Nevertheless, the *d*-band-width can be estimated from the interatomic distances. According to the moment rule,[63] one expects the bandwidth to vary as $\sqrt{z}\,t$, where z is the number of like atoms and t the average hopping integral. t is expected to vary like R^{-5}, where R is the Ni-Ni distance. Since NiGa is isostructural with NiAl, the *d*-band-width for NiGa can be estimated from that for NiAl, and the lattice constants for NiAl (Ref. 64) (2.886 Å) and NiGa (Ref. 65) (2.8952 Å). The W value for NiGa thus obtained is 2.5 eV. However, if using the moment rule to calculate W for NiGa from the lattice constant of Ni (3.52 Å), one would obtain 1.1 eV, which is unreasonably small. This suggests that the distance variation of t is less rapid than R^{-5}, and further suggests that hybridization between Ni *d* and Ga *p* orbitals is important. In the limit $W/Q \rightarrow 0$, the splitting of the main band and satellite is Q, and I_{sat} is roughly given by $n_h/(1-n_h)$, where n_h is the number of holes in the *d* band.[60] The Q value for NiGa in this atomic limit is about 6.2 eV on resonance, and about 6.8 eV off resonance. For the other limit $Q/W \rightarrow 0$, there will be no bound state, and the spectrum will consist of one asymmetric line.[66] For cases with an immediate value of W/Q, it is difficult to obtain an exact expression for the line shape. However, for $Q > W$ (as in the case for NiGa), a bound state will still exist and the I_{sat} value will depend on $n_h/(1-n_h)$, but will be reduced from this value.[67] The reduction is a function of the W/Q value, band filling, and band degeneracy.[60] For simplification of the discussion, we assume that the Q's for Ni and Ni compounds are large compared with the corresponding W values, i.e., in the $W/Q \rightarrow 0$ limit. Thus the n_h values for Ni and Ni compounds can be estimated, and are listed in the last column in Table I. One can see that the satellite intensity is strongest for Ni metal, which has 0.5 holes per Ni atom. This n_h value equals the *d*-band occupancy used by Victora and Falicov[68] in their exact calculation of the Ni density of states (DOS) within the context of a full many-body scheme, and is only 10% smaller than the theoretical[69] and experimental[70] estimates of 0.56 *d* hole per Ni atom for Ni metal. It should be also noted that Bosch *et al.*[60] reported I_{sat} and n_h values of $(130 \pm 20)\%$ and 0.57, respectively, for 5% Ni in Au, in which Ni as a dilute impurity forms a very narrow (0.2-eV FWHM) virtual bound state about 0.45 eV below E_F. We thus have a high degree of confidence in the procedures followed and assumptions made in determining n_h values for other Ni compounds. With a decreasing hole concentration in the Ni compounds in Table I, the corresponding I_{sat} values decrease. For NiGa, the I_{sat} and n_h values are 49% and 0.33, respectively. These values are compared with those of 13% and 0.12 for Cu metal.[6,53] It is generally believed that satellites in the spectra of Cu vapors and Cu metal are due mostly to the final-state effect,[22] since (1) the initial-state ($3d^9 4s^2$ and $3d^{10} 4s$) configuration mixing is not appreciable, and (2) I_{sat} does not vary much for different initial states for Cu vapors and Cu metal. For metallic compounds NiTe and NiSb, the resonances of satellites and main 3*d* bands are weaker compared with Ni metal, which is explained by the smaller number of *d* holes in these compounds.[22,71] For NiS, the satellite is very weak due to the large number of *d* holes (1.7 holes per Ni atom) resulting from the Ni 3*d*–S 3*sp* hybridization.[72] One point that must be made more strongly here is that the different resonance behaviors of the satellite structures in the Ni compounds are partly due to differences in the electronegativity values and partly and more importantly due to different $3p \rightarrow 3d$ and $3d \rightarrow \varepsilon f$ transition probabilities resulting from the different *d*-electron numbers. This point has also been mentioned in the study of the 3*d* transition-metal dichlorides.[20] Therefore, it is not surprising that I_{sat} and n_h values in Table I do not correlate with the corresponding electronegativity values.

The effective Coulomb interaction of two holes at the same site, U_{eff}, is given by[73]

$$U_{\text{eff}} = E_{B,s} - 2E_{B,d} \ , \tag{5}$$

where $E_{B,d}$ and $E_{B,s}$ are the binding energies of the *d*-band maximum and the satellite, respectively. The U_{eff} value for NiGa thus obtained from the data of Hsu and Williams[32] is 4.6 eV off resonance and 5.3 eV on resonance. However, this estimate of U_{eff} carries some uncertainty due to the well-known multiplet structures in the *d*-band and satellite structures. However, if the major peak of the multiplets is taken, a reasonable value of U_{eff} can be obtained. The off-resonance value for NiGa is surprisingly close to that of 4.3 eV used by Victora and Falicov[64] in the calculation of total and angle-resolved DOS's for Ni. A value $U_{\text{eff}} = 4.3$ eV was used by them because good agreement between the calculated total DOS (Ref. 64) and XPS spectra[74] was found not only in the existence and in the fitted position of the satellite, but also in its relative intensity and in the 3*d*-band-width. In the copper oxide system,[53] U_{eff} changes with *d*-band filling; while in the nickel silicide system,[26] U_{eff} is almost the same and essentially equals to the elemental Ni value of about 4.6 eV. That U_{eff} does not change appreciably from Ni to its silicides was also observed by Bisi *et al.*[75] in the study of XPS and Auger spectra of the nickel silicide system. It is worthwhile mentioning here that the U/Q ratio for NiGa (0.68 off resonance, 0.85 on resonance) is very close to that assumed (0.7) for the heavy-transition-metal dihalides.[76,77] This is not unreasonable since the U/Q ratio is essentially independent of ligands because U and Q are mostly determined by atomic parameters. The similarity between NiGa and Ni can be made more clear by plotting U_{eff} and $2W$ versus atomic numbers for the metals Fe, Co, Ni, Cu, Zn, Ga, and Ge, as was done by Antonides, Janse, and Sawatzky.[78] We see that NiGa should be placed near Ni, and that these two curves cross in the vicinity of Ni. This observation is the third indication that the Ni d band is not completely filled in NiGa.

The conclusions drawn from this study are (1) configuration mixing between $3d^84s^2$ and $3d^94s$ initial states contributes significantly to the satellite structure in NiGa; (2) the strong $3d$-band resonance for NiGa is due to the $3d^84s$ final state ($3d^94s$ initial state); (3) hybridization between Ni d and Ga p orbitals is more important than that between Ni d and Ga d orbitals; (4) the number of holes per Ni atom in the Ni d band for NiGa is estimated to be 0.33; (5) the effective Coulomb interaction between two $3d$ hole on the same site is 4.6 eV off resonance and 5.3 eV on resonance; and (6) the Ni d band in NiGa is not completely filled.

We would like to thank B. Alavi for making the sample and D. Outka and R. S. Williams for the support during the experiment. This research was partially supported by the National Science Council, Taiwan, ROC under Grant No. NSC 83-0208-M-018-001, and was partially done at SSRL, which is supported by the U. S. Department of Energy, Office of Basic Energy Sciences.

---

[*] Electronic address: phhsu@ncue4680.ncue.edu.tw

[1] U. Fano, Phys. Rev. **124**, 1866 (1961); U. Fano and J. W. Cooper, Rev. Mod. Phys. **40**, 441 (1968).

[2] C. Guillot, Y. Ballu, J. Paigne, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Petroff, and L. M. Falicov, Phys. Rev. Lett. **39**, 1632 (1977).

[3] S. C. Wu, C. K. C. Lok, J. Sokolov, F. Jona, and A. Taleb-Ibrahimi, Phys. Rev. B **39**, 1058 (1989).

[4] L. C. Davis, J. Appl. Phys. **59**, R25 (1986).

[5] D. R. Penn, Phys. Rev. Lett. **42**, 921 (1979).

[6] M. Iwan, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. **43**, 1829 (1979).

[7] M. Iwan, E. E. Koch, T.-C. Chiang, and F. J. Himpsel, Phys. Lett. **76A**, 177 (1980).

[8] T.-C. Chiang and D. E. Eastman, Phys. Rev. B **21**, 5749 (1980).

[9] D. Chandesris, G. Krill, G. Maire, J. Lecante, and Y. Petroff, Solid State Commun. **37**, 187 (1981).

[10] J. Barth, F. Gerken, K. L. J. Kobayaski, J. H. Weaver, and B. Sonntag, J. Phys. C **13**, 1369 (1980).

[11] D. Chandesris, J. Lecante, and Y. Petroff, Phys. Rev. B **27**, 2630 (1983).

[12] H. Sugawara, K. Naito, T. Miya, A. Kakizaki, I. Nagakura, and T. Ishii, J. Phys. Soc. Jpn. **53**, 279 (1984).

[13] H. Sugawara, A. Kakizaki, I. Nagakura, and T. Ishii, J. Phys. F **12**, 2929 (1982).

[14] H. Kato, T. Ishii, S. Masuda, Y. Harada, T. Miyano, T. Komeda, M. Onchi, and Y. Sakisaka, Phys. Rev. B **32**, 1992 (1985).

[15] D. Chandesris, J. Lecante, and Y. Petroff, Phys. Rev. B **34**, 8971 (1986).

[16] H. Kato, T. Ishii, S. Masuda, Y. Harada, T. Miyano, T. Komeda, M. Onchi, and Y. Sakisaka, Phys. Rev. B **34**, 8973 (1986).

[17] L. C. Davis and L. A. Feldkamp, Phys. Rev. Lett. **44**, 673 (1980); Phys. Rev. B **23**, 6239 (1981).

[18] A. Franciosi, S. Chang, R. Reifenberger, U. Debska, and R. Riedel, Phys. Rev. B **32**, 6682 (1985).

[19] K. E. Smith and V. E. Henrich, Phys. Rev. B **38**, 9571 (1988).

[20] A. Kakizaki, K. Sugeno, T. Ishii, H. Sugawara, I. Nagakura, and S. Shin, Phys. Rev. B **28**, 1026 (1983).

[21] A. Kakizaki, T. Miya, K. Naito, I. Fukui, H. Sugawara, I. Nagakura, and T. Ishii, J. Phys. Soc. Jpn. **54**, 3638 (1985).

[22] S.-J. Oh, J. W. Allen, I. Lindau, and J. C. Mikkelsen, Jr., Phys. Rev. B **26**, 4845 (1982).

[23] M. R. Thuler, R. L. Benbow, and Z. Hurych, Phys. Rev. B **27**, 2082 (1983).

[24] J. W. Allen, W. P. Ellis, L. E. Cox, B. B. Pate, R. D. Cowan, M. B. Maple, I. Lindau, Y. Laissailly, G. A. Sawatzky, and J. Zaanen (unpublished).

[25] W. P. Ellis, R. C. Albers, J. W. Allen, Y. Laissailly, J.-S. Kang, B. B. Pate, and I. Lindau, Solid State Commun. **62**, 591 (1987).

[26] H. Daimon, A. Ishizaka, K. L. I. Kobayashi, and Y. Murata, J. Phys. Soc. Jpn. **53**, 2130 (1984).

[27] T. Miyahara, T. Hanyu, H. Ishii, H. Kataura, M. Yanagihara, A. Fujimori, T. Koide, and H. Kato, J. Phys. Soc. Jpn. **58**, 2160 (1989).

[28] W. Gordy and W. J. O. Thomas, J. Chem. Phys. **24**, 439 (1956).

[29] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, NY, 1960), Chap. 3.

[30] E. Sacher and J. F. Currie, J. Electron Spectrosc. Relat. Phenom. **46**, 173 (1988).

[31] A. R. Miedema, F. R. de Boer, and P. F. de Chatel, J. Phys. F **3**, 1558 (1973).

[32] L.-S. Hsu and R. S. Williams, Phys. Lett. A **178**, 192 (1993).

[33] J. P. Neumann, Scr. Met. **11**, 969 (1977); Y. Xu, M. Ghafari, H. Hahn, U. Gonser, and B. Molnar, Solid State Commun. **61**, 779 (1987).

[34] L.-S. Hsu, Ph.D. thesis, University of California, Los Angeles, 1988.

[35] D. Heskett, I. Strathy, E. W. Plummer, and R. A. de Paola, Phys. Rev. B **32**, 6222 (1985).

[36] J.-J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[37] F. Greuter, D. Heskett, E. W. Plummer, and H.-J. Freund, Phys. Rev. B **27**, 7117 (1983); D. Heskett, I. Strathy, E. W. Plummer, and R. A. de Paola, *ibid.* **32**, 6222 (1985).

[38] L.-S. Hsu and R. S. Williams, J. Phys. Chem. Solids **55**, 305 (1994).

[39] J. M. McKay and V. E. Henrich, Phys. Rev. B **32**, 6764 (1985).

[40] A. Seiler, C. S. Feigerle, J. L. Pena, R. J. Celotta, and D. T. Pierce, Phys. Rev. B **32**, 7776 (1985).

[41] P. H. Holloway, J. Vac. Sci. Technol. **18**, 653 (1981); S. Masuda, M. Nishijima, Y. Sakisaka, and M. Onchi, Phys. Rev. B **25**, 863 (1982).

[42] E. Bertel, R. Stochbauer, and T. E. Madey, Phys. Rev. B **27**, 1939 (1983); Surf. Sci. **141**, 355 (1984).

[43] G. B. Fisher and B. A. Sexton, Phys. Rev. Lett. **44**, 683 (1980); T. E. Madey and F. P. Netzer, Surf. Sci. **117**, 549 (1982).

[44] R. L. Kurtz and V. E. Henrich, Phys. Rev. B **26**, 6682 (1982); **28**, 6699 (1983).

[45] L.-S. Hsu (unpublished).

[46] E. W. Plummer and W. Eberhardt, Adv. Chem. Phys. **49**, 533 (1982), and references therein.

[47] D. Heskett, E. W. Plummer, R. A. de Paola, W. Eberhardt, F. M. Hoffmann, and H. R. Moser, Surf. Sci. **164**, 490 (1985).

[48] N. D. Shinn and T. E. Madey, Phys. Rev. B **33**, 1464 (1986).

[49] F. Greuter, I. Strathy, E. W. Plummer, and W. Eberhardt, Phys. Rev. B **33**, 736 (1986).

[50] J. Barth, G. Kalkoffen, and C. Kunz, Phys. Lett. **74A**, 360 (1979).

[51] G. P. Williams, G. J. Lapeyre, J. Anderson, F. Cerrina, R. E. Dietz, and Y. Yafet, Surf. Sci. **89**, 606 (1979).

[52] Y. Sakisaka, T. Komeda, M. Onchi, H. Kato, S. Masuda, and K. Yagi, Phys. Rev. Lett. **58**, 733 (1987).

[53] M. R. Thuler, R. L. Benbow, and Z. Hurych, Phys. Rev. B **26**, 669 (1982).

[54] A. Kakizaki, H. Sugawara, I. Nagakura, Y. Ishikawa, T. Komatsubara, and T. Ishii, J. Phys. Soc. Jpn. **51**, 2597 (1982).

[55] S. Hufner, G. K. Wertheim, and J. H. Wernick, Solid State Commun. **17**, 417 (1975).

[56] R. E. Dietz, E. G. McRae, Y. Yafet, and C. W. Caldwell, Phys. Rev. Lett. **33**, 1372 (1974).

[57] L. C. Davis and L. A. Feldkamp, Solid State Commun. **19**, 413 (1976).

[58] A. Kakizaki, J. Fujii, K. Shimada, A. Kamata, K. Ono, K.-H. Park, T. Kinoshita, T. Ishii, and H. Fukutani, Phys. Rev. Lett. **72**, 2781 (1994).

[59] Y. Yafet, Phys. Rev. B **21**, 5023 (1980).

[60] A. Bosch, H. Feil, G. A. Sawatzky, and N. Martensson, Solid State Commun. **41**, 355 (1982).

[61] D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. **40**, 1514 (1978); F. J. Himpsel, J. A. Knapp, and D. E. Eastman, Phys. Rev. B **19**, 2919 (1979); W. Eberhardt and E. W. Plummer, *ibid.* **21**, 3245 (1980).

[62] S.-C. Lui, J. W. Davenport, E. W. Plummer, D. M. Zehner, and G. W. Fernando, Phys. Rev. B **42**, 1582 (1990).

[63] F. Cyrot, Adv. Phys. **16**, 393 (1967).

[64] H. Jacobi and H.-J. Engell, Acta Metall. **19**, 701 (1971).

[65] K. Ho, M. A. Quader, F. Lin, and R. A. Dodd, Scr. Met. **11**, 1159 (1977).

[66] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).

[67] L. C. Davis and L. A. Feldkamp, J. Appl. Phys. **50**, 1944 (1979).

[68] R. H. Victora and L. M. Falicov, Phys. Rev. Lett. **55**, 1140 (1985).

[69] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[70] H. Dannan, R. Heer, and A. J. P. Meyer, J. Appl. Phys. **39**, 669 (1968).

[71] J. W. Allen and J. C. Mikkelsen, Jr., Phys. Rev. B **15**, 2952 (1977).

[72] A. Fujimori, K. Terakura, M. Taniguchi, S. Ogawa, S. Suga, M. Matoba, and S. Anzai, Phys. Rev. B **37**, 3109 (1988).

[73] J. C. Parlebas, A. Kotani, and J. Kanamori, Solid State Commun. **41**, 439 (1982).

[74] S. Hufner and G. K. Wertheim, Phys. Lett. **51A**, 299 (1975).

[75] O. Bisi, C. Calandra, U. del Pennino, P. Sassaroli, and S. Valeri, Phys. Rev. B **30**, 5696 (1984).

[76] J. Zaanen, C. Westra, and G. A. Sawatzky, Phys. Rev. B **33**, 8060 (1986).

[77] J. Park, S. Ryu, M.-S. Han, and S.-J. Oh, Phys. Rev. B **37**, 10 867 (1988).

[78] E. Antonides, E. C. Janse, and G. A. Sawatzky, Phys. Rev. B **15**, 1669 (1977).