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VALENCE-BAND AND CORE-LEVEL PHOTEMISSION SATELLITES IN NiGa

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Photoemission studies of the valence-band and core-level satellites of NiGa are presented. The valence-band satellite is resonantly enhanced near the 3p threshold ($h\nu = 67eV$), and its centroid position is photon energy dependent, which is in agreement with previous observations for elemental Ni. Surprisingly, the resonantly enhanced valence-band satellite in NiGa has about the same intensity as that for elemental Ni, even though the number of empty d-states contributing to the resonant enhancement is expected to be smaller in NiGa.

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Valence-Band and Core-Level Photoemission Satellites in NiGa Intermetallic Compound

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Photoemission studies of the valence-band and core-level satellites of NiGa are presented. The valence-band satellite is resonantly enhanced near the 3p threshold (hv =67eV), and its centroid position is photon energy dependent, which is in agreement with previous observations for elemental Ni. Surprisingly, the resonantly enhanced valence-band satellite in NiGa has about the same intensity as that for elemental Ni, even though the number of empty d-states contributing to the resonant enhancement is expected to be smaller in NiGa.

Valence-band and core-level satellites observed in ultra-violet and X-ray photoelectron spectroscopy (UPS and XPS) studies of elemental Ni have been the subject of many experimental[1-6] and theoretical[7-11] investigations in the last decade. The valence-band satellite is resonantly enhanced near the $3p \rightarrow 3d$ excitation threshold,[1] and its centroid moves with photon energy (hv).[12] The existence of these satellites is related to the fact that Ni has a partially filled d band (0.6 hole per Ni atom), which allows the creation of a two-hole bound state on some Ni atoms after a photoionization event.[7,8,11] The resonant enhancement of the valence-band satellite is caused by the interference of two excitation channels leading to the same final state. One channel is the $3p^6 3d^9 \rightarrow 3p^5 3d^{10}$ photoexcitation followed by a super-Coster-Kronig (sCK) transition. The other channel is the nonresonant shake-up process proposed by Penn.[7] The recently characterized phenomenon of the apparent shift in energy of the valence-band satellite with hv has been interpreted in terms of different contributions of the singlet and triplet satellite states, which occur at different energies, for on- and off-resonance excitation conditions.[12]

Several studies have characterized the photon energy dependences of the Ni satellite feature in compounds such as NiO^4 and NiAs.[?] In the compounds studied to date, the Ni has been the less electronegative species. Thus, the occupation of the d-states should be less than in elemental Ni. In the cases studied, the valence-band satellite was still present and it exhibited resonant behavior very similar to that for Ni metal. This paper presents a resonant photoemission study of NiGa, a compound in which there should be some electron transfer to the Ni atoms

from the less electronegative Ga, and thus a higher occupation of the d-states. The intent of this study was to see what effect a decrease in the hole concentration of the d-band would have on the Ni *photoemission* satellite and its resonant behavior.

Polycrystalline NiGa was prepared from weighed amounts of 99.999 at. % pure Ni and Ga by arc melting under 1 atm argon. It was then annealed in an evacuated quartz tube at 750 °C for 50 hours and quenched in a water bath. The total loss of weight during these processes was about 1 % . Powder X-ray diffractometry showed that the sample was a single phase and of the CsCi structure.

The XPS data for NiGa were collected with a Kratos ES 800 equipped with a nonmonochromatic Mg Kα (hν =1253.6 eV) X-ray source and a 150mm hemispherical electron energy analyzer. The UPS experiments were carried out on beam line VIII-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). Photon energies in the range of 30 to 160 eV were selected with a toroidal grating monochromator, and a PHI 15-255 G double-pass cylindrical mirror analyzer (CMA) was used in the constant-pass energy mode to collect the photoelectron spectra. The resolution for XPS and UPS was about 0.7 eV and 0.5-0.8 eV, respectively. The working pressures in the XPS and UPS chambers were 1×10^{-10} Torr and 8×10^{-9} Torr, respectively. The NiGa surface was cleaned by repeated cycles of argon ion bombardment and annealed to 350 °C for 15 minutes. The XPS spectra were free of any detectable contamination by O or C, but the sample from which UPS data were obtained had about 3% of a monolayer (ML) of O and 6% ML of C, as estimated from Auger spectra collected with the CMA.

Fig. 1 shows energy distribution curves (EDC's) of NiGa for 60 eV$\leq$ hv $\leq$ 80 eV. The binding energy (E_B) is referred to the Fermi energy (E_F), and all the spectra are normalized to equal intensity at the maximum of the Ni 3d-band emission, which consisted of only one peak at 0.8 eV E_B. The satellite at ~6eV below the Ni 3d peak is enhanced near the 3p threshold (hv =67 eV). The observation that the satellite shifts in binding energy with hv is consistent with a previous study of elemental Ni.[12] The satellite peak position is observed at ~6.2 eV below the Ni 3d peak away from resonance and shifts to ~6.9 eV below the Ni 3d peak on resonance (67 eV$\leq$ hv $\leq$ 70 eV). Sakisaka et. al.[12] estimated the shift to be ~1 eV in elemental Ni, which is comparable to our value of 0.7 eV. The expected peak positions of the $M_{2,3}VV$ Auger transition, which are only observed at hv $\geq$ 68 eV, are marked by arrows in Fig. 1.

The appearance of an Auger peak can be seen more clearly from the difference spectra shown in Fig. 2. The difference spectra in Fig. 2(a) were obtained by subtracting the EDC at hv =64eV from EDC's at higher hv, i.e. N(hv)-N(64eV), 67eV $\leq$ hv $\leq$ 76eV. The $M_{2,3}VV$ Auger transition, which is marked by arrows in Fig. 2, appears above hv =68eV and can be seen as a higher binding energy shoulder in N(68 eV)-N(64 eV) and a broader structure in N(hv)-N(64 eV), where 70eV $\leq$hv $\leq$ 76 eV. The intensity of the $M_{2,3}VV$ Auger emission at hv =67 eV should be essentially zero, so in N(67 eV)-N(64 eV) there is only one feature corresponding to the extra enhancement of the higher binding-energy part of the satellite (^{1}G configuration). In Fig. 2(b), we subtract the EDC at hv =67eV from EDC's at hv =68, 70, and 72 eV. The $M_{2,3}VV$ Auger emission shows a peak in N(68eV)-N(67eV) and a broader structure in N(70eV)-N(67eV) and in

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N(72eV)-N(67eV). Compared with the satellite peak position of the EDC at hv =67eV, one can see that the dips in these difference spectra represent the resonant enhancement of the satellite. From these difference spectra, we can separate the contribution of the incoherent Auger emission from that of the coherent Auger-type decay in the resonance-enhanced satellite structure. Also, if there is any spurious structure in the spectra caused by O or C contamination on the sample surface, we can cancel their contributions in these difference spectra. The enhancement of the satellite at resonance is thus shown to be not caused by the incoherent Auger emission but to be due to the coherent sCK-type decay.

The intensity of the satellite peak at hv =67eV is about 64 % of the Ni 3d peak in NiGa, which is comparable to the value ($\sim$60 %) obtained by Chandesris et. al.[13] for the resonantly-enhanced satellite intensity in elemental Ni. This is an indication that the Ni d-band is still not filled in NiGa. We will come to this point later when discussing the XPS data.

Fig. 3 shows Ni 2p XPS spectra for NiGa after subtracting a smooth background using Shirley's method.[14] The binding energies of the Ni $2p_{1/2}$ and $2p_{3/2}$ levels and their respective satellites are shown in Table 1 along with those of elemental Ni, NiAl, and NiIn.[15] We determine the satellite intensity the same way as was done in ref 15 in order to compare our results with theirs.

The electronegativities of Al, In, and Ga are essentially the same.[16] If Ni core-level satellite intensities in 1:1 compounds have a general trend with partner eletronegativity,[15] the intensity of the satellite feature (I_{sat}) for NiGa should be about the same as those for NiAl and NiIn. This is evident from the Ni $2p_{3/2}$ satellite intensities in Table 1.

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The Ni $2p_{1/2}$ satellite in NiGa has a much broader structure than the Ni $2p_{3/2}$ satellite, so the determination of its I_{sat} is more uncertain than that for the Ni $2p_{3/2}$ satellite. The results for NiGa are in reasonable agreement with NiAl and NiIn, as shown in Table 1.

Since no shake-up satellite of the Ga 3d core peak was observed in either UPS or XPS spectrum, the two-hole bound state, which is responsible for the occurrance of the satellite feature in NiGa, is actually localized at the same Ni atom, i.e. it is the intra-atomic Coulomb interaction that forms the two-hole bound state. In other words, transfer of a hole from Ga 3d to Ni 3d is very inefficient in NiGa.

It is worth noting that ΔE for the $2p_{3/2}$ line is larger than that for the $2p_{1/2}$ line in Ni and the NiM (M=Al, Ga, In) intermetallic compounds. Bosch et. al.[6] explained this phenomenon as the result of the suppression of the multiplet lines closest to the main $2p_{3/2}$ line, while the $2p_{1/2}$ satellite structure corresponds to the configuration averaged position as calculated by Martensson and Johansson.[17]

Hillebrecht et. al.[15] attributed the decreasing of the satellite intensity in Ni alloys to d band filling. However, this argument requires further analysis. In the UPS study, we observed roughly the same resonant satellite to 3d peak intensity ratio in NiGa as in elemental Ni. If the Ni d band is filled in NiGa, the final state of the 3p→nl excitation is either 4sp state[8] or the unoccupied state with d character[15] (due to s-d hybridization). In either case, the resonant satellite intensity in NiGa should be expected to be much less than that in elemental Ni. Analogies are found in the UPS studies of Zn[18] and Cu;[2] the former has a resonant satellite to 3d peak intensity ratio of only 6%, while that of the latter has

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12%. This difference was explained by the fact that Zn has a completely filled d band, while Cu has only about 0.4 d-holes per Cu atom that result from s-d hybridization. Spin-polarized photoemission and inverse photoemission studies on the Ni-group III intermetallic compounds should help in understanding the transitions responsible for the Ni satellite ferture more completely.

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Table 1. Binding energies of Ni $2p_{1/2}$, $2p_{3/2}$ levels and satellites in Ni, NiAl, NiGa, and NiIn (in eV).

	$2p_{3/2}$ BE[a]	ΔE[b]	I_{sat}[c]	$2p_{1/2}$ BE[a]	ΔE[b]	I_{sat}[c]	Chemical[d] shift
Ni[e]	852.65	5.8±0.4	29	869.90	4.6±0.4	28	
NiAl[e]	852.80	7.2±0.4	19	870.10[f]	5.65±0.4	23	0.20
NiGa	853.00[f]	6.3±0.6	17	870.10[f]	5.1±0.6	27	0.27
NiIn[e]	852.35	6.7±0.3	20	869.55	5.45±0.5	25	-0.30

a. Uncertainty ±0.2eV unless otherwise stated.

b. Binding energy difference between main line and satellite; satellite has larger binding energy.

c. Satellite intensity as percent of total intensity of main line plus satellite. Uncertainty ±2%.

d. BE(intermetallic compound)- BE(Ni), averaged over 2p lines.
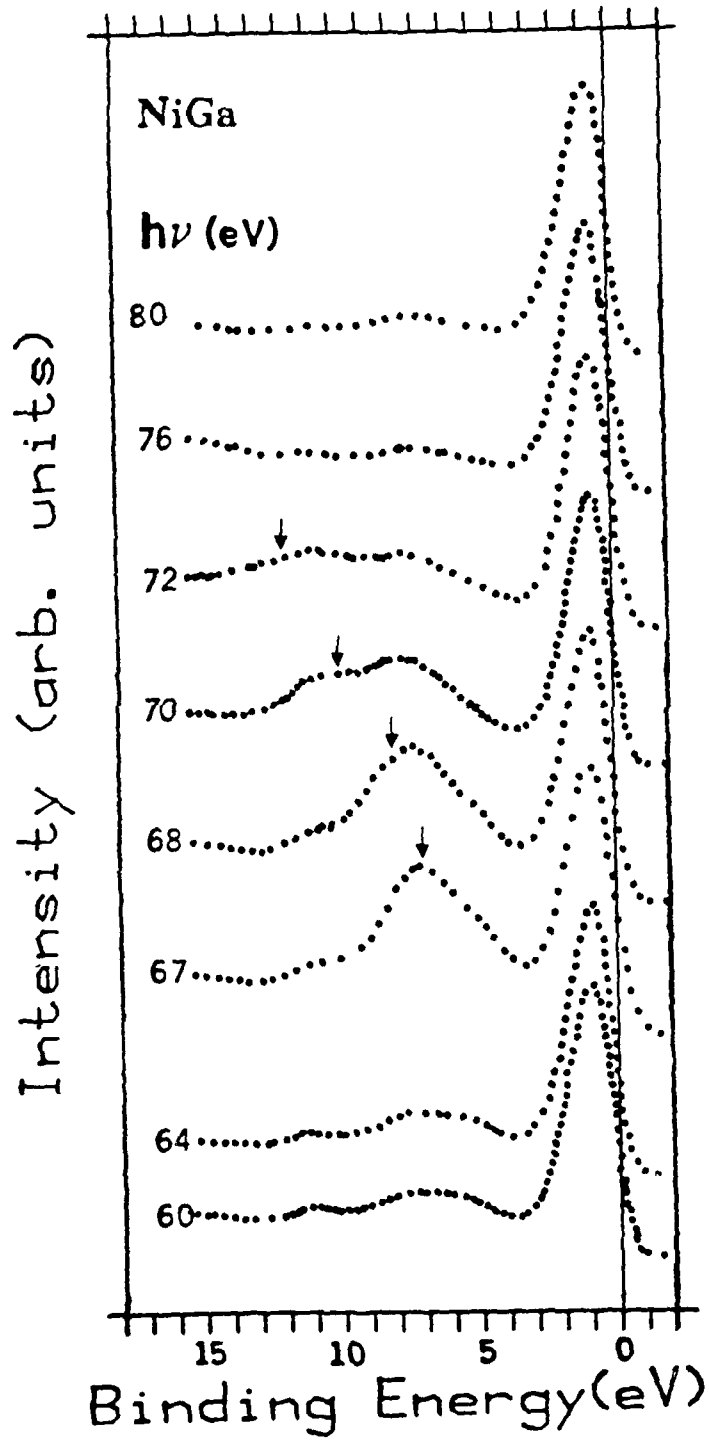
e. Data taken from ref. 15.

f. Uncertainty ±0.3 eV.

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FIGURE CAPTIONS

Fig. 1. Photoemission spectra of NiGa measured at 60eV $\leq h\nu \leq$ 80 eV. The arrows indicated the expected peak positions of the $M_{2,3}VV$ sCK line.
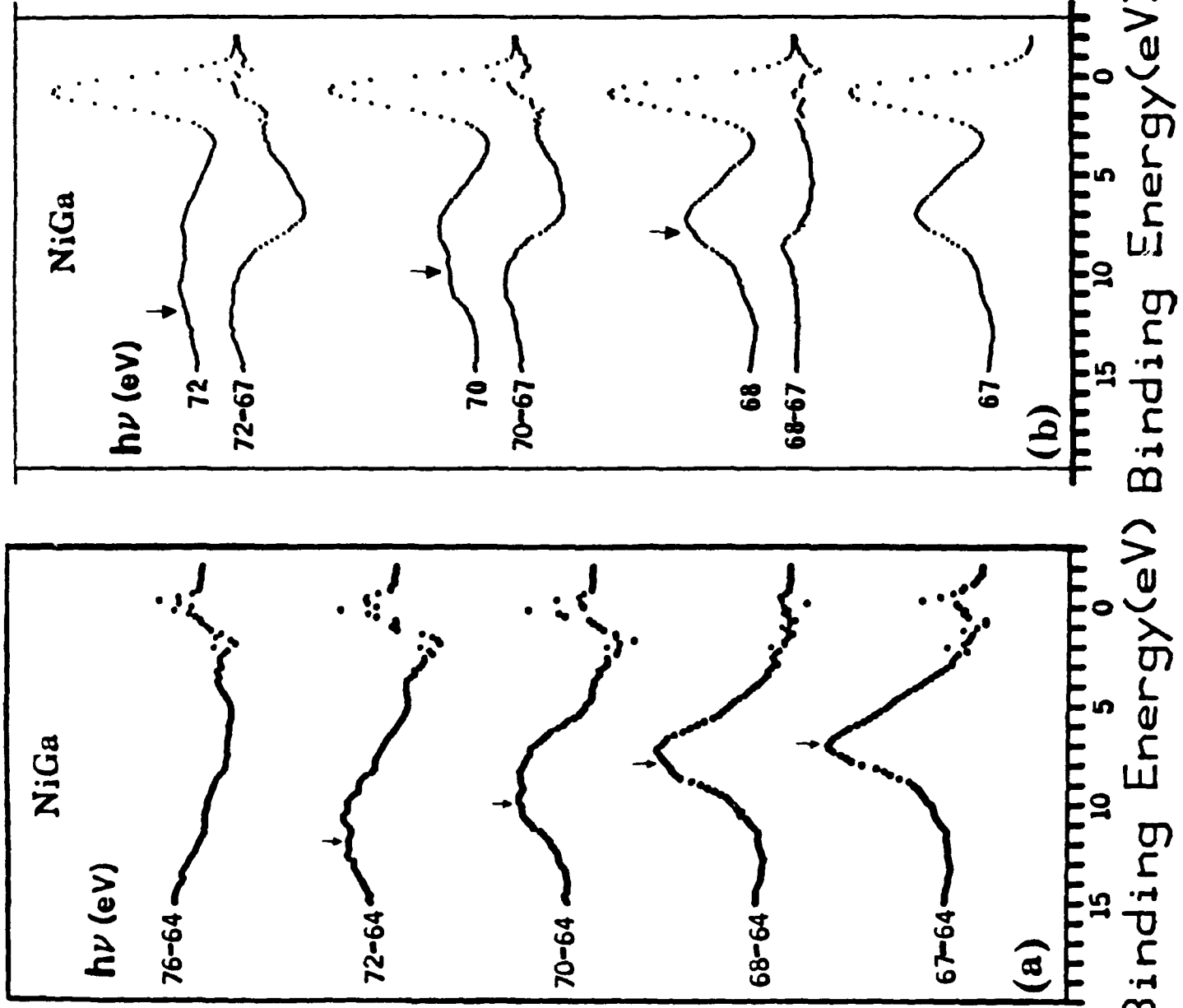
Fig. 2. (a) Selected difference spectra $N(h\nu)-N(64eV)$ of the EDC's of NiGa. The expected positions of the $M_{2,3}VV$ sCK line are indicated by arrows.

(b) Selected difference spectra $N(h\nu)-N(67eV)$ of the EDC's of NiGa. For comparison, the corresponding EDC's are also shown above each difference spectrum. The expected positions of the $M_{2,3}VV$ sCK line are indicated by arrows.

Fig. 3. Ni 2p XPS spectra of NiGa. The spectrum was recorded with 0.1eV stepwidth, and a smooth background has been subtracted.

NiGa

hν (eV)

80

76

72

70

68

67

64

60

Intensity (arb. units)

Binding Energy (eV)

15 10 5 0

NiGa

$h\nu$ (eV)

72

72-67

70

70-67

68

68-67

67

(b)

Binding Energy(eV)

NiGa

$h\nu$ (eV)

76-64

72-64

70-64

68-64

67-64

(a)

Binding Energy(eV)

Intensity (arb. units)

Binding Energy(eV)

NiGa

$2p_{3/2}$

$2p_{1/2}$

Intensity (arb. units)

Binding Energy (eV)

845   855   865   875   885