Observation of Conduction Band Satellite of Ni Metal by 3p-3d Resonant Inverse Photoemission Study

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Resonant inverse photoemission spectra of Ni metal have been obtained across the Ni 3p absorption edge. The intensity of Ni 3d band just above Fermi edge shows asymmetric Fano-like resonance. Satellite structures are found at about 2.5 and 4.2 eV above Fermi edge, which shows resonant enhancement at the absorption edge. The satellite structures are due to a many-body configuration interaction and confirms the existence of 3d⁸ configuration in the ground state of Ni metal.

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Inverse photoemission spectroscopy (IPES) is an important technique to investigate the unoccupied density of states (DOS) of a solid. Combining photoemission spectroscopy (PES), which measures the occupied DOS, with IPES measurements, gives us complementary information about the valence and conduction band DOS. The IPES technique has two measurement modes: Bremsstrahlung Isochromat Spectroscopy (BIS) mode and Tunable Photon Energy (TPE) mode. The BIS measurements are easier than TPE measurements, because it does not use a photon monochromator and sensitive band pass filters are available in X-ray and vacuum ultraviolet (VUV) region. This has led to the early development of X-ray BIS (XBIS) and ultra-violet BIS (UVBIS) techniques.

The observation of IPES in the soft X-ray (SX) region corresponding to energies from several ten’s of eV to about 1 keV is still experimentally difficult, because the emission intensity in XPE is extremely weak. We succeeded in the observation of the resonant IPES (RIPES) of Ce compounds near the Ce 4d absorption region, using a monochromator developed for SX emission spectroscopy (SXES). The obtained results are consistent with Ce 3d RIPES by Weibel et al., though the surface effect is strong. Furthermore, RIPES of Ti compounds was also measured across the Ti 3p edge and a weak satellite has been found.

Ni metal is an itinerant ferromagnet which has been used as a classic reference to test the validity of new experimental and theoretical techniques in the study of electronic structure of solids. Beginning with the Stoner condition in the mean-field approximation or the local density approximation (LDA), as well as many spectroscopic studies of Ni metal have provided important insights in the study of solids e.g. resonant PES,¹²,¹³, angle-resolved PES,¹⁴ magnetic circular dichroism (MCD),¹⁵,¹⁶ and spin-resolved PES.¹⁷,¹⁸,¹⁹ Furthermore, UVBIS and XBIS spectra of Ni metal have also been reported, as well as spin polarized and k-resolved IPES. The observed electronic structure of Ni is, however, still an important subject of study that many researchers are interested in, since it is not understood within standard band theory and only recent dynamical mean field studies provide a consistent description of its magnetic properties and electronic structure.

It is well known that the so-called “6-eV satellite” is observed in the PES spectrum at about 6 eV from Fermi energy Eₚ.¹¹,¹⁷ This satellite is known as the two-hole-bound state that means two 3d holes are bound in the same Ni site in the final state, and has a 3d⁸ final state (3d⁹ initial state). Another satellite was found at a higher energy than 6 eV and it was assigned to the 3d⁸ final state (3d⁹ initial state).³⁰ Furthermore, it was suggested by analysis of the MCD spectra that the 3d⁸ configuration with ³F symmetry exists with a weight of 15 to 20 % in the ground state. Sinkovic et al. found triplet feature of 3d⁸ configuration at 6 eV by means of spin-resolved PES.³¹

The main 3d configuration of Ni atom in Ni metal is 3d⁹ in the ground state. From a many-body view-point, 3d¹⁰ and 3d⁸ should be mixed in addition to 3d⁹ due to the electron transfer. Then, the ferromagnetism is considered to be caused by Hund’s coupling in the 3d⁸ configuration as it reduces the energy cost of an electron transfer. In fact, such a viewpoint is proposed as an origin of ferromagnetism in Ni. In this context, an experimental measurement of 3d⁸ weight is of great importance.

In this study, we report resonant IPES of Ni metal across the Ni 3p-absorption edge. Since the process of the IPES adds an electron to the ground state, IPES should give us new information of the ground state configuration.

Figure 1 shows energy diagram of RIPES. In a normal IPES process, an electron that is incident upon a solid surface decays radiatively to states at lower energy. In a 3d⁰-electron system, the normal IPES process is expressed as

\[ \beta d^m \rightarrow e + \beta d^{m+1} \rightarrow n + h\nu \]  \hspace{1cm} (1)

where e denotes incident electron. If the electron energy is higher than the binding energy of a core level, the core electron can be excited and ejected out of the system. Then, the created core-hole decays radiatively (fluorescence) or non-radiatively (Auger process). The fluorescence process is

\[ \beta d^m \rightarrow \beta d^{m-1} + h\nu \]  \hspace{1cm} (2)
Pressure was measuring $O_1$ about $14 \text{ K}$. The cleanliness of the sample was checked by torr. Measurements were performed at low temperature of grating (300 lines/mm), was used in this experiment.

A soft X-ray monochromator, which consists of a Rowland-type grazing-incidence monochromator with a 5-m spherical type grazing-incidence monochromator with a 5-m spherical grating, was used in this experiment. The incidence angle of monochromator was fixed at an angle of $30^\circ$. Measurements were performed at low temperature of about $14 \text{ K}$. The cleanliness of the sample was checked by measuring $O_1$s fluorescence. The measurement chamber was checked by measuring $O_1$s fluorescence. The measurement chamber pressure was $< 1 \times 10^{-8} \text{ torr}$ throughout the measurements. Single crystal was measured with some excitation energies. (110) sample was cleaned by Ar-ion bombardment and annealing. The cleanliness was checked by Auger and LEED measurements.

A filament-cathode-type and a BaO-cathode-type electron guns were used for excitation. The kinetic energy of excitation electron was calibrated by an energy analyzer. An excitation electron was incident normally for polycrystal, while off-normal for Ni(110), because of experimental arrangement. The emission was observed at an angle of about $60^\circ$. The overall spectral resolution of this measurement was about $0.6 \text{ eV}$ at excitation energy of $60 \text{ eV}$. The spectra were normalized by emission of electron gun and $h \nu^3$, since the cross section of emission spectra is proportional to third power of photon energy.

Figure 2 shows RIPES spectra of polycrystalline sample, obtained for various energies across the Ni $3p$ absorption edge. Numbers beside the spectra indicate excitation energies. In this figure, observed spectra, which have energies close to excitation energies, are plotted with respect to the relative energy from Fermi edge. The spectrum of $54.0 \text{ eV}$, which is observed near the absorption edge. Insertion shows the intensity of RIPES features. The filled circles and squares show the intensity of Ni $3d$ main peak and Ni $4sp$, respectively. The solid lines were obtained by smoothing, plotted as a guide for eyes. The open squares and triangles show calculated intensity of main peak and satellite, respectively.

When the excitation energy is higher than $66.1 \text{ eV}$, a core fluorescence peak is observed at a constant energy of about $66 \text{ eV}$ in emission spectra. The energy position of this peak is observed near the absorption edge. Insertion shows the intensity of Ni $3d$ main peak and Ni $4sp$, respectively. The solid lines were obtained by smoothing, plotted as a guide for eyes. The open squares and triangles show calculated intensity of main peak and satellite, respectively.

The Ni $3d$ peak is also observed just above $E_F$, Ni $4sp$ peak is also observed at about $10 \text{ eV}$. Dotted lines denote the satellite structures observed near the absorption edge. Insertion shows the intensity of Ni $3d$ main peak and Ni $4sp$, respectively. The solid lines were obtained by smoothing, plotted as a guide for eyes. The open squares and triangles show calculated intensity of main peak and satellite, respectively.
by vertical bars. The Ni 3d peak just above $E_F$ becomes very weak when the excitation energy is around 66.1 eV, where the fluorescence peak has almost same emission energy. On the other hand, Ni 4sp peak does not seem to change its intensity with changing excitation energy. In addition to these structures, a weak structure is observed at around 2.5 and 4.2 eV as indicated by the dotted line. These structures are observed only at the excitation near absorption edge.

Insertion in Fig. 2 shows the peak intensity of the Ni 3d and Ni 4sp peak plotted versus the excitation energy. Filled circles and squares denote the intensity of Ni 3d and Ni 4sp, respectively. The open squares and triangles are calculated intensity that is discussed below.

The Ni 3d spectrum has a dip at about 66 eV and shows an asymmetric lineshape typical of a Fano-type resonance. A similar resonance has been observed in the resonant photoemission study of Ni. On the other hand, the Ni 4sp peak does not change its intensity with changing excitation energy, although at higher energies it cannot be conclusively stated because of an overlap with the fluorescence signal. Thus, satellite intensity is observed at about 58 eV.

The results show that the IPES of Ni 3d exhibits a resonance effect at the excitation energy near Ni 3p-absorption edge. The nominal ground state of Ni is 3d9 configuration. It is thought, however, that the actual ground state consists of a mixture of 3d8, 3d9 and 3d10 configurations. The intermediate state of RIPES has an n+2 electron state as has been mentioned before. So, only the 3d8 initial state can be resonant in the IPES process, while the 3d9 and 3d10 initial states cannot resonate. That is, the observed resonance confirms the existence of 3d8 configuration in the ground state. The existence of 3d8 configuration has been suggested by resonant PES and MCD measurements. However, the present result is the only direct experimental evidence of a 3d8 initial-state configuration.

Figure 3 shows comparison between on- and off-resonant spectra. The spectra of (110) single crystal are shown in addition to the on-resonant spectrum of polycrystal. The spectra of single crystal show narrower main peak than that of polycrystal, because these were observed in angle resolved mode. In the on-resonance spectra of both samples, two satellite structures are observed at about 2.5 and 4.2 eV as indicated by the dotted lines, while the off-resonant spectrum does not show. A fluorescence component is expected in the on-resonance spectrum at the energy position marked by arrow in Fig. 3, but it is very weak compared with other structures. The spectrum at bottom shows the calculation result discussed in the following.

We now discuss the origin of the satellite structures. We think the satellite structures are not caused from k-dependence of other components, because Ni 4sp peak is observed broadly in both sample at around 10 eV that is sufficiently higher than the satellite energy. Possibility of direct transition that is observed in UVBIS spectra can be neglected, because the excitation energy in this study is much higher than UVBIS.

Since the satellites are observed near absorption edge, it is possible that the structure is caused by a many-body effect, as suggested by Tanaka and Jo. The spectrum at bottom of Fig. 3 shows RIPES spectra of Ni metal calculated by impurity Anderson model including many-body configuration interaction effect. In the calculation, the initial state of Ni metal consists of 3d8, 3d9 and 3d10 configurations, and the IPES spectrum consists of the three structures arising from the bonding, non-bonding and anti-bonding states of the 3d8 and 3d10 configurations. The main peak near Fermi edge corresponds to the bonding state and it shows Fano-type resonance, while non-bonding and anti-bonding peaks at 2.5 and 4.2 eV are resonantly enhanced at absorption edge. In this calculation, band effect is not included. If proper band effect is included in this calculation, the non-bonding peak would become wide as observed in experimental results. The intensity changes in this calculation are shown in Fig. 2. The calculated results seem to qualitatively well-describe the intensity change of main peak. From the comparison between the observed and calculated spectra, the weight of 3d8 in Ni metal is estimated to be at least 10 %.

As mentioned before, a satellite called the "two-hole-bound state" is observed at 6 eV in resonant PES spectra. The satellite arises from 3d8 dominant states, while the main peak corresponds to 3d9 dominant states. The non-bonding state is not observed in PES spectra. The satellite energy of 6 eV in PES is larger than that of RIPES in this study. This is attributed to the fact that the satellite in PES has 3d8 configuration and Coulomb interaction between two holes is more effective, while the satellite in RIPES has 3d9 configuration. Furthermore, in case of PES spectra that have 3d8 and 3d9 final states, the multiplet splitting of the 3d8 configuration is larger than the hybridization energy, so that the separation of
the anti-bonding state from the non-bonding $3d^8$ state is not obvious. On the other hand, there is no multiplet splitting due to Coulomb interaction in the final states of IPES, because the final states have $3d^9$ and $3d^{10}$ configurations. Thus, the non-bonding state would become observable in IPES.

In conclusion, we could observe RIPES spectra of Ni metal across the Ni $3p$-$3d$ absorption edge. Satellite structures of Ni $3d$ band are observed at about 2.5 and 4.2 eV. The excitation spectrum of Ni $3d$ state shows Fano type resonance across the Ni $3p$ absorption edge. The results are a direct evidence for existence of $3d^8$ configuration in the initial state of Ni metal. The satellites are described well by the cluster-model calculation including many-body configuration interaction effects. This result must help for understanding the ferromagnetism on Ni metal.

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