Conduction band satellite of Ni metal observed using 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 show 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 ultraviolet 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 IPE is extremely weak. We succeeded in the observation of the resonant IPES (RIPES) of Ce (Refs. 4 and 5) 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 (Refs. 8 and 9) 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, angle-resolved PES, magnetic circular dichroism (MCD), and spin-resolved PES. 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 $E_F$. 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 (3d8 initial state). Another satellite was found at a higher energy than 6 eV and it was assigned to the 3d7 final state (3d8 initial state). Furthermore, it was suggested by analysis of the MCD spectra that the 3d8 configuration with $^1F$ symmetry exists with a weight of 15%-20% in the ground state. Sinkovic et al. found triplet feature of 3d8 configuration at 6 eV by means of spin-resolved PES.

The main 3d configuration of Ni atom in Ni metal is 3d8 in the ground state. From a many-body viewpoint, 3d10 and 3d8 should be mixed in addition to 3d8 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 3d-electron system, the normal IPES process is expressed as

$$3d^n + e^- \rightarrow 3d^{n+1} + h\nu,$$

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 nonradiatively (Auger process). The fluorescence process is
FIG. 1. Energy diagram of RIPES. At low energy excitation, only normal IPES is observed. If the excitation is higher than an absorption edge, a core hole is created which decays by fluorescence. Near an absorption edge, RIPES process can take place.

\[ |\epsilon 3d^p\rangle \rightarrow |3d^{p-1}\rangle + h\nu, \] (2)

where \( \epsilon \) denotes core hole. On the other hand, if the energy of the incident electron is close to the Ni 3p \( \rightarrow \) 3d absorption edge, a second order process:

\[ |3d^p\rangle + e^- \rightarrow |3p^23d^{p+2}\rangle \rightarrow |3d^{p+1}\rangle + h\nu \] (3)

would take place. Because of the interference between Eqs. (1) and (3), a resonance effect would be observed.

IPES measurements of Ni were performed on both polycrystal and (110) single crystal. The polycrystalline sample was evaporated on Mo substrate at a pressure of \( < 1 \times 10^{-8} \) Torr. Measurements were performed at low temperature of about 14 K. The cleanliness of the sample was checked by measuring O 1s fluorescence. The measurement chamber pressure was \( < 3 \times 10^{-10} \) 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 soft x-ray monochromator, which consists of a Rowland-type grazing-incidence monochromator with a 5-m-spherical grating (300 lines/mm), was used in this experiment. The incidence angle of monochromator was fixed at an angle of 85.98°. Two types multichannel detector PIAS (for wide range) and CR-chain (for high resolution) (Hamamatsu photonics) were used as a photon detector. The absolute energies of the spectra were calibrated by measuring the Fermi edge of Au.

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°.

FIG. 2. RIPES spectra of Ni metal. The dots show observed spectra and solid lines were obtained by smoothing. The numbers beside the spectra denote the excitation energy. The excitation energy in each spectrum are shown by vertical bars, which correspond to Ni 3d \( \rightarrow \) 3p fluorescence in the high energy spectra. Ni 3d IPES peak is observed just above \( E_F \). Ni 4sp peak is also observed at about 10 eV. Dotted lines denote the satellite structures observed near the absorption edge. Inset shows the intensity of IPES features. The filled circles and squares show the peak intensity of Ni 3d main peak and Ni 4sp, respectively. The filled triangles and open circles show the intensity of satellite and Ni 3d \( \rightarrow \) 3p fluorescence, 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 overall spectral resolution of this measurement was about 0.6 eV at excitation energy of 60 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 the 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 eV, which is sufficiently below the absorption edge, corresponds to normal IPES spectrum. This spectrum agrees with the spectra observed in XBIS\(^{20}\) and UVBIS.\(^{21}\) From comparison with band calculations, the structure just above Fermi edge and broad peak at about 10 eV are assigned to Ni 3d and Ni 4sp bands, respectively.

When the excitation energy is higher than 66.1 eV, a core electron is excited. Thus, the emission spectrum then includes both IPES and fluorescence components. The Ni 3d \( \rightarrow \) 3p fluorescence peak is observed at a constant energy of about 65 eV in emission spectra. The energy position of this peak is changed with changing excitation energy in Fig. 2 as...
indicated 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 the 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.

The inset in Fig. 2 shows the intensity of the IPES peaks plotted versus the excitation energy. Filled circles and squares denote the peak intensity of Ni 3d and Ni 4sp, respectively. The filled triangles and open circles denote the intensity of the satellites and Ni 3d $\rightarrow$ 3p fluorescence, respectively. These intensities were obtained by rough estimation under the assumption that the IPES of Ni 3d and Ni 4sp have the same line shapes in every spectra. The open squares and triangles are calculated intensity that is discussed below.\textsuperscript{35} The Ni 3d spectrum has a dip at about 66 eV and shows an asymmetric line shape typical of a Fano-type resonance.\textsuperscript{30} A similar resonance has been observed in the resonant photoemission study of Ni.\textsuperscript{12,30} 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. The satellites are observed in the spectra excited by 58–68 eV. The satellites seem to be enhanced at the resonance, though the Ni 3d $\rightarrow$ 3p fluorescence over the satellite in some spectra.

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 3d\textsuperscript{9} configuration. It is thought, however, that the actual ground state consists of a mixture of 3d\textsuperscript{8}, 3d\textsuperscript{9}, and 3d\textsuperscript{10} configurations. The intermediate state of RIPES has an n+2 electron state as has been mentioned before so, only the 3d\textsuperscript{8} initial state can be resonant in the IPES process, while the 3d\textsuperscript{9} and 3d\textsuperscript{10} initial states cannot resonate. That is, the observed resonance confirms the existence of 3d\textsuperscript{8} configuration in the ground state. The existence of 3d\textsuperscript{8} configuration has been suggested by resonant PES\textsuperscript{30} and MCD\textsuperscript{11,32} measurements. However, the present result is the only direct experimental evidence of a 3d\textsuperscript{8} 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 the bottom shows the calculation result\textsuperscript{35} 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\textsuperscript{35} 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.\textsuperscript{35} 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 3d\textsuperscript{8}, 3d\textsuperscript{9}, and 3d\textsuperscript{10} configurations, and the IPES spectrum consists of the three structures arising from the bonding, nonbonding and antibonding states of the 3d\textsuperscript{8} and 3d\textsuperscript{10} configurations. The main peak near Fermi edge corresponds to the bonding state and it shows Fano-type resonance, while nonbonding and antibonding 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 nonbonding 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 and satellites. From the comparison between the observed and calculated spectra, the weight of 3d\textsuperscript{8} 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 3d\textsuperscript{9} dominant states, while the main peak corresponds to 3d\textsuperscript{8} dominant states. The nonbonding 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 3d\textsuperscript{8} configuration and Coulomb interaction between two holes is more effective, while the satellite in RIPES has 3d\textsuperscript{9} configu-
ration. Furthermore, in the case of PES spectra which have 3d$^8$ and 3d$^9$ final states, the multiplet splitting of the 3d$^8$ configuration is larger than the hybridization energy, so that the separation of the antibonding state from the nonbonding 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$^8$ and 3d$^{10}$ configurations. Thus, the nonbonding 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 the Ni 3d band are observed at about 2.5 and 4.2 eV.

The excitation spectrum of the Ni 3d state shows Fano-type resonance across the Ni 3p absorption edge. The results are direct evidence for existence of 3d$^8$ configuration in the initial state of Ni metal. The satellites are described by the cluster-model calculation including many-body configuration interaction effects. This result helps, in understanding the ferromagnetism on Ni metal.

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