新博士紹介

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6. **Title**: Photoemission experiments in rare earth compounds and magnetic thin films: Study of the electron correlation effects

The photoemission experiments have been performed for some mixed valent rare earth compounds (TmX, X=S, Se and Te) and thin films of 3*d*-transition metals (Ni and Co) to study the effects of the electron correlation in the photoemission spectra. In the rare systems, some interesting phenomenon, such as nature of core hole-4*f*-shells interaction, multiplet structures, resonant enhancement of multiplets, lifetime broadening, configuration interaction, valence fluctuation were examined and explained by comparing with calculated results. In the transition metal thin film system Ni/Co/Cu(001), the resonance effect on magnetic dichroism (MD) signal for the correlation induced Ni 6 eV-satellite was studied around Ni3*p* threshold. Magnetic dichroism (MD) is a novel technique based on photoemission by proper selecting of orientation of light polarization, directions of magnetization and electron emission. In the present study, magnetic properties for Ni/Co/Cu(001) system was studied by analyzing the MD signal for Ni3*d* at Ni3*p* resonant condition and for Ni-, Co-3*p* photoemission.

Because of the valence fluctuation, TmS, TmSe and TmTe show mostly trivalent, typical intermediate valent and mostly divalent characteristics, respectively. Similar to 4*f* resonant photoemission reported by Y. Ufukete *et al.*[1)], the 4*d* core level also shows the mixed valent properties[2)]. But in the 4*d* case, the components of Tm^{2+} and Tm^{3+} are largely overlapped in some certain binding energy ranges. Therefore the resonant photoemission is very much essential to separate the valence components.

In **Fig. 1**, the Tm4*d* RPES results at Tm3*d*-4*f* resonance are in TmS, the trivalent compound. The experiment was done in the x-ray beamline BL7A at the UVSOR facility. The modified VGESCALAB220i-XL photoelectron system[3)] with base pressure of 2×10^{-10} mbar was used for this purpose. **Figures 1**(a–d) show the on- and off-resonant 4*d* core level photoemission results. In **Fig. 1**(a), the XPS result by using MgKα line is also shown in order to make clearer the off-resonant spectral feature. The spectra show almost trivalent nature, but with small amount of the divalent component for all photoemission spectra. The excitation energies indicated by alphabet (A–D) are selected from the TY (total photoelectron yield corresponding to photoabsorption) spectrum shown in **Fig. 1**(e). It is noticed that the 4*d* spectra are enhanced very much (about 10 times of off-resonant one) under the 3*d*-4*f* resonant condition. The resonance effect of spectra in **Figs. 1**(b–d) is explained by considering the inter-

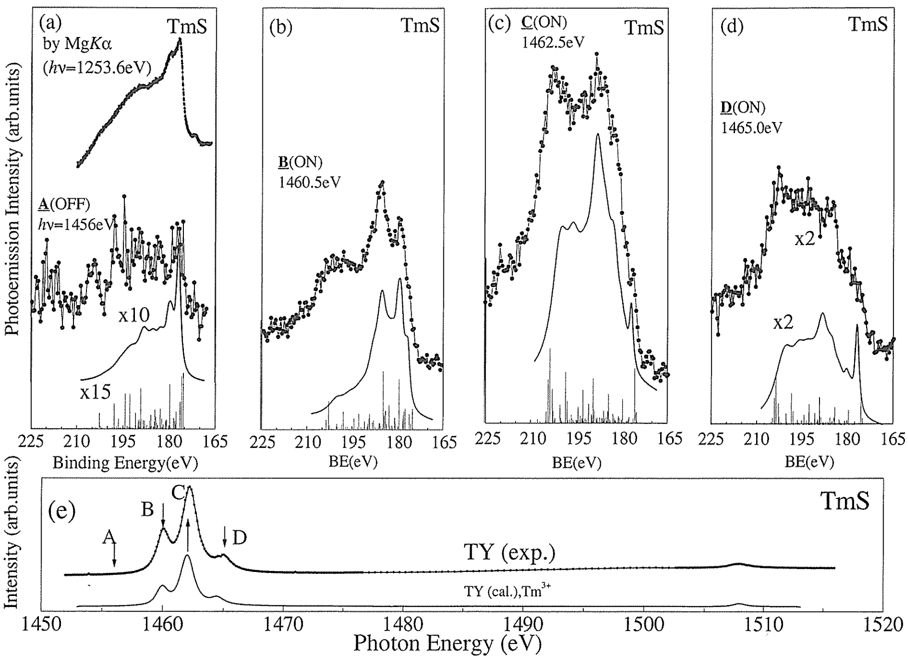

Figure 1. (a–d) Tm 4*d* resonant photoemission spectra of TmS. (a) shows the off-resonant spectrum along with the XPS spectrum excited by MgKα radiation. (b–d) show the on-resonant spectra. All solid curves represent the calculated for each resonance condition of the trivalent Tm ion.
(e) 3*d*-4*f* total photoelectron yield spectrum for mostly trivalent compound, TmS. The marks B, C and D indicate the resonance peak maxima, corresponding to the three resonant conditions of trivalent Tm ion and mark A shows off-resonant condition. The calculated absorption spectrum for trivalent Tm ion is also shown for comparison.

ference between the direct 4*d* photoemission and the 4*d* excitation to continuum state due to the decay channel, $3d^{10}4d^{10}4f^{12}+h\nu \rightarrow 3d^{9}4d^{10}4f^{13} \rightarrow 3d^{10}4d^{9}4f^{12}+\varepsilon l$.

In the figure, it is shown that some of the final states are considered to take part strongly in decay excitation process and show relatively stronger resonant enhancement due to the preferential decay channels of individual excited state. For example in **Fig. 1**(b), the spectrum at $h\nu=1460.5$ eV shows two dominant enhanced peaks with binding energies of ~180.5 eV and ~185.5 eV. Calculation also shows almost the same feature. In the second and third resonance conditions (at $h\nu=1462.5$ and 1465 eV, respectively), the higher binding energy parts are more enhanced than lower binding energy parts. This distinction of resonant effect in 4*d* multiplet peaks depends on the strength of relevant Auger decay of individual excited state. At the same time, the shape of both on- and off-resonant spectra is affected by the 4*d* core hole lifetime broadening effect. According to Ogasawara *et al.*[4], the lifetime broadening effect in the 4*d*-XPS varies strongly with the binding energy. In order to reproduce the spectra, the term dependent Lorentzian [$(\Gamma_f)=0.1(E_B-E_0)$ eV, where E_0 is the lowest binding energy] was used in the calculation for both the on- and off-resonant spectra. Even in the on-resonant condition where the different multiplets show different resonant enhancement, the concept of term dependent broadening effect is very satisfactory. Besides 4*d* photoemission, the 5*p* resonant photoemission at Tm4*d*-4*f* resonance, 4*p* XPS and 3d photoemission spectra were also measured.

The magnetic dichroism experiment for Ni/Co system[5] was carried in the beamline BL5B at the UVSOR facility using the same VG photoelectron system[3]. **Figure 2** shows the Ni thickness dependent Ni3*d* photoemission and the MLD (magnetic linear dichroism) results for Ni(8 ML)/Co(10 ML)/Cu(001) system. In **Fig. 2**(a), we show the photoemission spectra of valence band region for different thickness (n=ML) of Ni on Co(001) at 3*p*-3*d* resonant condition; $h\nu=67.2$ eV. The photoemission spectra except for n=0 show the two dominant peaks, the main peak (Ni3d^9) and the "6 eV-satellite" peak (Ni3d^8). This satellite peak shows a strong resonant enhancement at the 3*p*-excitation energy that was explained via super-Coster-Kronig (sCK) decay process[6]. In the inset, the saturation condition (~4.5 ML or 8 Å) for Ni growth is shown.

In **Figs. 2**(b) and (c), the MLD results for Ni(8 ML)/Co(10 ML)/Cu(100) taken at the photon energies of 67.2 eV (on-resonant) and 63 eV (off-resonant) are shown, respectively. In the upper panels [**Figs. 2**(b) and (c)], the two spectra represent the intensities for two different magnetized states (shown in inset), one is along to X-axis (full circle) and another is parallel to Y-axis (open circle). The lower panels in **Figs. 2**(b) and (c) show the asymmetry between those two spectra. The observed MLD signal indicates the in-plane magnetization of the Ni/Co(001) system.

In the lower panel of **Fig. 2**(b), both the main peak (3d^9) and the satellite peak (3d^8) show asymmetry (i.e., MLD) but in opposite direction to each other. In the previous study[7], Ueda and co-workers reported the results for MLDAD (AD=angular distribution) and MCDAD (C=circular) measurements for the bulk Ni(110) sample. In MLDAD, the 6 eV-satellite does not show any prominent MD signal whereas the main peak shows MD signal at 3*p*-excitation

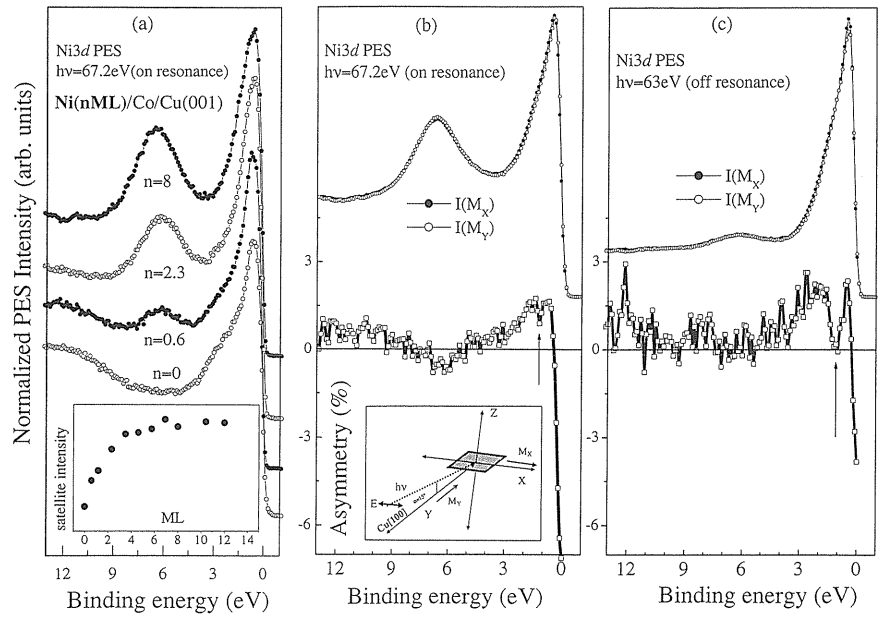

Figure 2. (a) Photoelectron intensities of Ni3*d* states for different thickness (n=ML) of Ni grown on Co(10ML)/Cu(001) at Ni3*p*-3*d* on resonant condition. The variation of 6 eV-satellite peak intensity as a function of Ni thickness is shown in inset.
(b) & (c) Photoemission spectra (upper part) and corresponding asymmetry (lower part) at on- and off-resonant conditions, respectively for 8 ML Ni on Co (10 ML).

threshold. On the other hand, the MCDAD is rather strong for both the 6 eV-satellite and the main peak with opposite sign. The present result is similar to that reported for the MCDAD result. The shape of asymmetry in the main peak is almost same for both the off-resonant condition in **Fig. 2**(c) and on-resonant condition in **Fig. 2**(b). But the dip structure (marked by arrow) at the binding energy of ~ 1.2 eV of off-resonant condition is stronger than that of on-resonant condition. Probably this variation may arise due to the photon energy dependence from different Ni3*d* states and the polarization effect on the MD signal. The asymmetry for satellite peak at off-resonance is not so strong as the on-resonance one, although it shows the opposite trend from the main peak. It can be interpreted that the 3*d*–3*p* resonant process mainly guides intensity of the asymmetry for 6 eV-satellite. It was not possible to estimate the contribution of dichroism signal from different multiplet peaks around the satellite region. In the thin film magnetism section of the thesis, the MLD for Ni–, Co-3*p* core level, electronic and magnetic structures of oxidized Co film were also reported.

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