Core level and Auger line shifts in CoPt alloys

Y. S. Lee, K. Y. Lim, Y. D. Chung, H. J. Kang,[1] and C. N. Whang

Atomic-scale Surface Science Research Center and Department of Physics, Yonsei University, Seoul 120-749, Korea
[1]Department of Physics, Chungbuk National University, Cheongju 361-763, Korea

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We investigated the x-ray photoelectron spectroscopy(XPS) core line and Auger line shifts in CoPt alloys. Upon alloying, the core electron states near valence band change but the core levels in the deeper state do not change. The Co $L_2M_{23}M_{45}$ and the Pt NNN Auger line shifts are larger than the Co $2p_{1/2}$ and the Pt $4f_{7/2}$ core level shifts, respectively. In addition, the Co $L_2M_{23}M_{45}$ Auger line shifts are larger than that of the Pt $N_{4,5}N_{6,7}N_7$ because the Co $L_2M_{23}M_{45}$ and the Pt $N_{4,5}N_{6,7}N_7$ Auger line shifts depend on three level changes($2p_{1/2}$, $3p$, and $3d$ states of Co) and two level changes($4f_{5/2}$ and $4f_{7/2}$ states of Pt), respectively.

1. Introduction

The CoPt alloys which is composed with the ferromagnetic $3d$ transition metal and paramagnetic $5d$ element, have attracted interest as both chemical stability and high magnetic anisotropy[1-3]. Since these magnetic properties must be ultimately related to the electronic structure of alloys, recently, there have been calculations and experiments to study the electronic structure of these alloy system[4-7].

Generally, it was known that upon alloying the valence states change is most dominant by the hybridization between neighboring atoms. So, in charge transfer between atoms, a charge change of the core-level states has been neglected. By W. F. Egelhoff [8], core level shift occurs due to Fermi level shift, an atomic volume change, the squeezing of valence electrons, the core-valence repulsion, the screening effects, and so on.

In order to understand the core level shifts and Auger line shifts of binary alloys, we employed x-ray photoelectron spectroscopy(XPS) and x-ray induced Auger electron spectroscopy(XAES) techniques.

2. Experiments

The Co_xPt_{1-x} (x = 0.25, 0.5, and 0.75) alloy samples were prepared by melting together carefully weighted amounts of starting metals in an arc furnace under an inert argon atmosphere. The melted samples of different compositions were separatedly sealed on evacuated quartz crucibles, and were given a homogenizing anneal at 1000 ℃ for 48 h after rolling into foils. At the end of the homogenizing anneal, these alloys were slowly cooled to room temperature. Characterization of the samples was carried out by x-ray diffraction. The structure of samples was confirmed to be ordered phase; $CoPt_3$ alloy of $AuCu_3$ type at x = 0.25, CoPt alloy of AuCu type at x = 0.5, and Co_3Pt alloy with *fcc* structure at x = 0.75.

Core level XPS spectra and x-ray induced Auger spectra of the sample surfaces were taken in PHI 5700 ESCA system with a hemispherical electron energy analyzer using Mg Kα (1253.6 eV) and monochromatic Al Kα (1486.7 eV) x-rays. The pass energy was 23.5 eV, giving an energy resolution of 0.7 eV to the Ag $3d_{5/2}$ line. The core-level binding energies were referenced to the Au $4f_{7/2}$ (= 84 eV) peak. The pressure of the analysis chamber during XPS measurements was maintained better than 2×10^{-10} Torr. Each samples were cleaned *in-situ* by Ar^+ ion bombardment to remove a contamination layers. The sputtering was done with the 3 keV Ar^+ ion beam (current ~1 μA) in the

pressure of 3×10^{-7} Torr. We used the bulk concentration because this alloy system is no surface segregation system[9] and this error would be very small.

3. Results and discussion

In Fig. 1(a), 1(b), and 1(c), we show the measured Co 2*p*, Co 3*p* and Co 2*s* core level spectra for pure Co and Co-Pt alloys, respectively. In Fig. 1(a), we can see the Co $2p_{1/2,3/2}$ core line peaks shift toward lower binding energy with increasing of the Pt concentration, even though the shifts are tiny. In addition, the Co 3*p* core line peaks shift also toward lower binding energy[Fig. 1(b)]. On the other hand, the Co 2*s* core level peaks[Fig. 1(c)] are not change nearly.

In Pt site, the Pt $4f_{5/2,7/2}$ core level peaks[Fig. 2(a)] shift toward higher binding energy with increasing of the Co content. In addition, the nearest core level peaks from the valence band, the Pt 5*p* peaks[Fig. 2(b)], shift toward also higher binding energy according to the increase of the Co concentration. On the other hand, the Pt $4d_{3/2,5/2}$ core level peaks[Fig. 2(c)] are not change nearly. By these results, we can see the core electron states near valence band change but the core levels in the deeper state do not change upon alloying. If a change of the valence states affects directly the core level shift, all core levels such as Co 2*s* and Co 1*s* must shift and the shifts must be same.

In physical standpoint, it is natural that upon alloying the valence states must change dominantly. Generally, the deeper a core level is, the more a relaxation energy is increased[11]. Therefore, an influences by a change of the valence states will decrease in a core level with the higher binding energy due to the screening effect. That is, it indicates that the deeper a core level is, the smaller a core level shift is. Than, we can explain the no change of the deeper core level upon alloying using this relaxation effect.

In a viewpoint of the free-atom-metal binding energy shifts, R. E. Watson *et al.*[12] reported that both 2*p* and 2*s* core levels in 3*d* transition metals shift. When it is transformed from free atom to metallic states, the

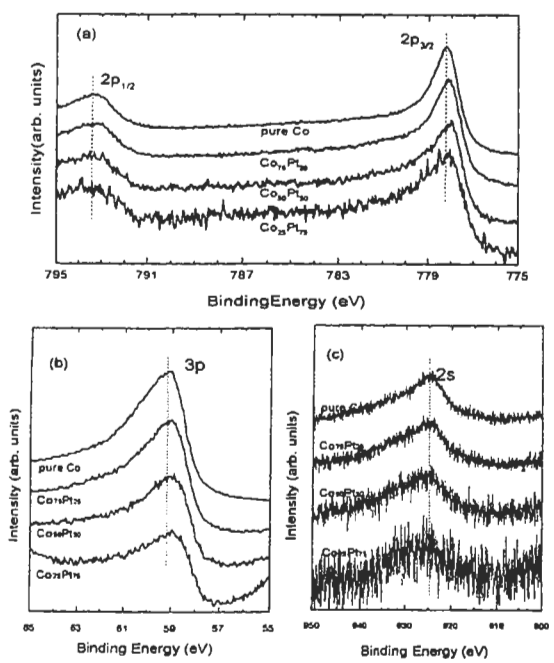

Figure 1. XPS core level spectra of (a) Co 2*p* by Mg Kα source, (b) Co 3*p* and (c) Co 2*s* states by Al Kα source in the pure Co and Co-Pt alloys. Using Al Kα source, the Co $2p_{3/2}$ peak is overlapped with the Co $L_3M_{23}M_{45}$ peak[10].

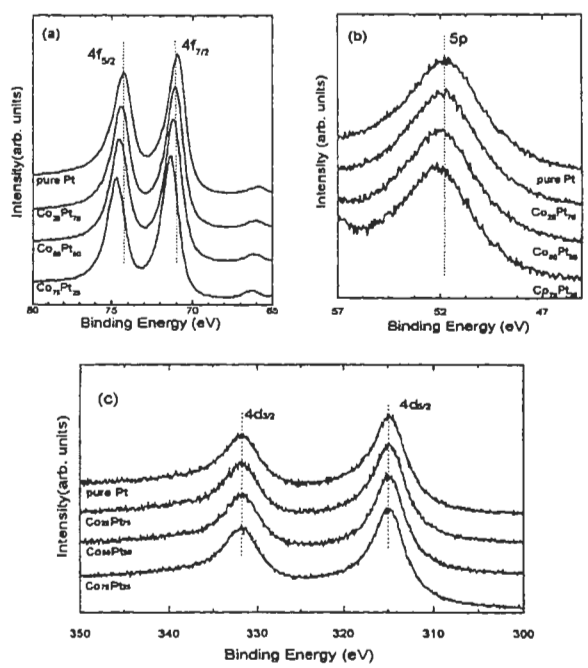

Figure 2. XPS core level spectra by Al Kα source of (a) Pt $4f_{7/2,5/2}$, (b) Pt 5*p*, and (c) Pt 4*d* states in the pure Pt and CoPt alloys.

core level shifts are very large (increasing to 11 eV for the Co $2p_{3/2}$ shift[13]), but upon alloying, the core level shifts are very small as shown in Fig. 1 and Fig. 2. Therefore, we can find that the deeper core level in alloys is not nearly influenced because the electronic structure change is very small upon alloying. We summarized these core level shifts of Pt and Co sites as a function of the Co concentration in Fig. 3.

We also measured the x-ray induced Auger line shifts as a function of the Co concentration[Fig. 4]. As shown in Fig. 4, the Co $L_2M_{23}M_{45}$ and the Pt $N_{4,5}N_{6,7}N_7$ Auger lines shift toward higher and lower kinetic energy

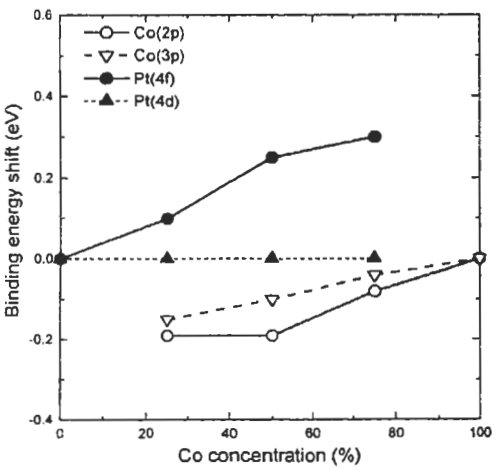

Figure 3. XPS core line shifts of Co $2p_{3/2}$, Co $3p$, Pt $4f_{7/2}$, Pt $4d$ states in Co-Pt alloys

with increasing of the Co concentration, respectively. As compare with the core level shifts[Fig. 3], the trends of shift direction are similar, that is, the Co $2p_{3/2}$ (and $3p$) and the Pt $4f_{7/2}$ core lines shift toward lower and higher binding energy with increasing of the Co concentration, respectively. On the other hand, the Co $L_2M_{23}M_{45}$ and the Pt $N_5N_{6,7}N_7$ Auger line shifts are larger than the Pt and Co core level shifts. Especially, the Co $L_2M_{23}M_{45}$ Auger line shifts are very large. In core level shifts[Fig. 3], the Pt $4f_{7/2}$ core shifts are larger than that of the Co $2p_{3/2}$ and/or $3p$, but in Auger line shifts[Fig. 4], the Co $L_2M_{23}M_{45}$ line shifts are larger than

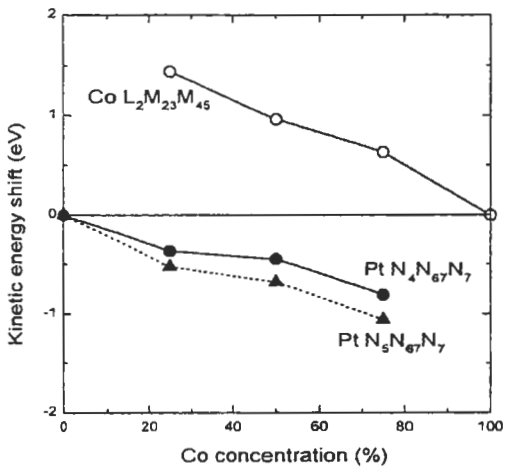

Figure 4. X-ray induced Auger line shifts of Co $L_2M_{23}M_{45}$ and Pt $N_{4,5}N_{6,7}N_7$ states in Co-Pt alloys.

the Pt $N_{4,5}N_{6,7}N_7$ Auger line shifts. What is the reason?

Figure 5 shows the Pt NNN Auger spectra. This NNN Auger transition[the right of Fig. 5] is not involved with the Pt $5d$ valence electrons. Only the $4d$ and $4f$ core electrons of Pt are involved. By the previous results of the Pt core level shift, the Pt $4d$ states did not change and the Pt $4f_{7/2,5/2}$ states changed upon alloying. After all, since the Pt NNN Auger line shifts depend on the change of both Pt $4f_{7/2}$ and $4f_{5/2}$ core states, the Pt NNN Auger line shifts are larger than the Pt $4f_{7/2}$ core line shifts upon alloying.

Figure 6 shows the Co $L_{2,3}MM$ Auger spectra and Auger transitions. The broad peak in ~789 eV is the $L_3M_{45}M_{45}$ Auger line. The Co $L_3M_{45}M_{45}$ transition is as the right-bottom of Fig. 6. This transition involves with the Co $3d$ electrons. However, this peak is very broad because Co has unfilled $3d$ shells. Nevertheless, we can see that these peaks clearly shift toward higher kinetic energy with increasing of the Pt concentration. The main peak in ~774 eV is a part by the $L_2M_{23}M_{45}$ Auger transition. These peaks also shift toward higher kinetic energy with increasing of the Pt content. This trend is different with a very little shift of the Co $2p_{1/2,3/2}$ or Co $3p$ core lines upon alloying. The $L_2M_{23}M_{45}$

transition comes from the $2p_{1/2}$ (L_2) core hole, relates to the Co $3p$ core(M_{23}) and the Co $3d$ valence(M_{45}) states as shown in the right-top of Fig. 6. According to the results of core levels, all of these three levels, that is, L_2(Co $2p_{1/2}$), M_{23}(Co $3p$), and M_{45}(Co $3d$), shifted upon alloying. Therefore, this Auger line shifts should be larger than the core line shifts. In addition, it is natural that the Co $L_2M_{23}M_{45}$ Auger line shifts are larger than that of the Pt $N_{4,5}N_{6,7}N_7$ because the Co $L_2M_{23}M_{45}$ and the Pt $N_{4,5}N_{6,7}N_7$ Auger line shifts depend on the change of three levels($2p_{1/2}$, $3p$, and $3d$ states of Co) and two levels($4f_{5/2}$ and $4f_{7/2}$ states of Pt), respectively.

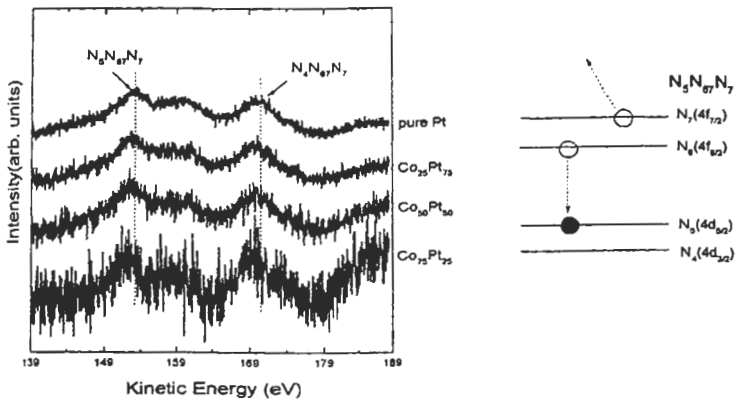

Figure 5. X-ray(Al Kα) induced Pt $N_{4,5}N_{6,7}N_7$ Auger line spectra of pure Pt and CoPt alloys.

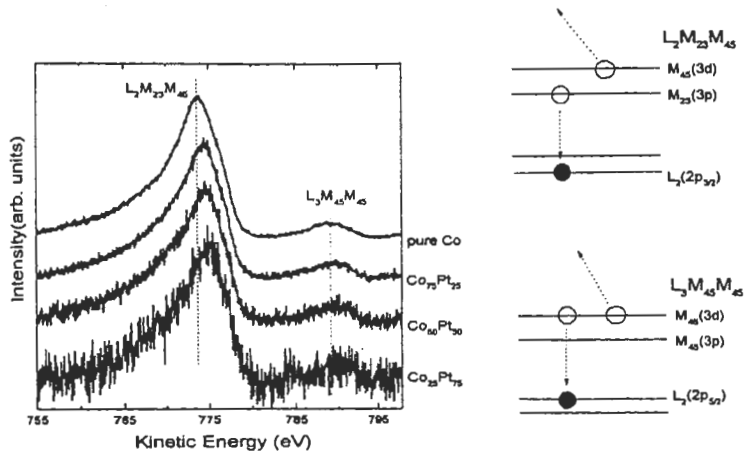

Figure 6. X-ray(Al Kα) induced Co $L_{2,3}MM$ Auger line spectra of pure Co and CoPt alloys.

Core-level binding energy and Auger energy shifts are related to changes in relaxation energy[11,14]. For species A in the A_xB_{1-x} alloy, the sum of a core level binding energy shift, $\triangle B^A$, and a core-core-core Auger energy shift, $\triangle K^A$, provides an estimate of the final state contributions to chemical shifts as follows[14].

$$\triangle B^A(x) + \triangle K^A(x) \approx 2\triangle E_R^A(x)$$

where, $\triangle E_R$ is the core-hole relaxation energy shift. The measured chemicals shifts in $\triangle B$, $\triangle K$, and $\triangle E_R$ for Co-Pt alloys relative to the corresponding elemental metals are summarized in Table 1. In order to estimate the $2p$ core hole relaxation energy, $\triangle E_R^{Co}$, we used the Co $2p$ core line shifts and the Co $L_2M_{23}M_{45}$(core $2p_{1/2}$ - core $3p$ - valence $3d$) Auger shifts because the $2p_{1/2}$ core level shifts was similar to the $2p_{3/2}$ core level shifts as shown in Fig. 1(a) and the Co $L_3M_{23}M_{23}$ Auger peaks in alloys are overlapped with the Co $L_2M_{23}M_{23}$ Auger peaks and the Pt $4p_{1/2}$ core peaks. Since the Co M_{45} states are unfilled and delocalized, the use of the Co $L_2M_{23}M_{45}$ Auger peak is possible although this Auger line has the core-core-valence Auger transition. In addition, to estimate the $4f$ core hole relaxation energy, $\triangle E_R^{Pt}$, we used the

Table 1. The core level binding energy, $\triangle B$[eV], the Auger kinetic energy, $\triangle K$[eV], and the relaxation energy, $\triangle E_R$[eV] shifts for Co-Pt alloys. x is Pt concentration.

Alloys	$\triangle B^{Pt}(x)$	$\triangle K^{Pt}_{N_4NN}(x)$	$\triangle E_R^{Pt}(x)$	$\triangle B^{Co}(x)$	$\triangle K^{Co}_{L_2MM}(x)$	$\triangle E_R^{Co}(x)$
$Co_{75}Pt_{25}$	0.30	-0.81	-0.255	-0.08	0.63	0.053
$Co_{50}Pt_{50}$	0.25	-0.45	-0.100	-0.19	0.96	0.385
$Co_{25}Pt_{75}$	0.10	-0.37	-0.135	-0.19	1.44	0.625

Pt 4*f* core line shifts and the Pt $N_4N_{6,7}N_7$ (core 4*d* - core 4*f* - core 4*f*) Auger line shifts. From the results in Table 1, we can confirm that the Co 2*p* core level shifts are smaller than that of the Pt 4*f* because the Co core hole relaxation energy shifts, $|\triangle E_R^{Co}|$, are larger than $|\triangle E_R^{Pt}|$ of Pt.

4. Conclusion

We have performed the XPS and x-ray induced AES study of the Co-Pt alloys to understand a relationship between core level line shifts and their Auger line shifts. Upon alloying, the core electron states near valence band change, but the core levels in the deeper state do not change. By our results, the Co 2*p* and Co 3*p* (and Pt 4*f* and Pt 5*p*) core levels near valence states shift, but the Co 2*s* and Pt 4*d* core levels with higher binding energy don't shift. This reason may be that the deeper core level in alloys is not nearly influenced because of the relaxation energy of core level site and the small charge change upon alloying.

In core level, the Co 2*p* core level shifts are smaller than the Pt 4*f* and in Auger line, the Co LMM Auger line shifts are larger than that of the Pt NNN. In addition, Auger line shifts are larger than the Co 2*p* and Pt 4*f* core line shifts.

Since the Pt $N_{4,5}N_{6,7}N_7$ Auger line shifts depend on only the Pt $4f_{5/2,7/2}$ core states change, the Pt NNN Auger line shifts are larger than the Pt $4f_{7/2}$ core line shifts upon alloying. Since the Co $L_2M_{23}M_{45}$ Auger line shifts depend on the three core level change, that is, Co $2p_{1/2}$, Co 3*p* and Co 3*d* states, the Co $L_2M_{23}M_{45}$ Auger line shifts are larger than the Co $2p_{1/2}$ core level shifts. In addition, it is natural that the Co $L_2M_{23}M_{45}$ Auger line shifts are larger than that of the Pt $N_{4,5}N_{6,7}N_7$ because the Co $L_2M_{23}M_{45}$ and Pt $N_{4,5}N_{6,7}N_7$ Auger line shifts depend on three level changes ($2p_{1/2}$, 3*p*, and 3*d* states of Co) and two level changes ($4f_{5/2}$ and $4f_{7/2}$ states of Pt), respectively.

Finally, we can find that the core level shifts is related to the Auger line shifts.

Acknowledgement

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5. References

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