

Photoemission Spectroscopic Study on the Electronic Structure of Fe-Pt Alloys

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We investigated the electronic structure of $\text{Fe}_x\text{Pt}_{1-x}$ ($x = 0.25, 0.5, 0.75$) alloys by photoemission spectroscopy by using synchrotron radiation. The Fe $3d$ and Pt $5d$ partial spectral weights are determined by taking advantage of the Cooper minimum phenomenon of Pt $5d$ photoionization cross section and taking the matrix element effect into consideration. Comparison with the previous band calculations is discussed.

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I. INTRODUCTION

The Fe-Pt alloy system has many interesting features. It forms a solid solution over a wide compositional range in a face-centered-cubic structure, has three well-defined intermetallic phases, and shows a martensitic transformation at lower Fe concentration. The ordered alloys are Fe_3Pt and FePt_3 of $L1_2$ structure and FePt of $L1_0$ structure [1,2]. Fe_3Pt is one of the best known Invar materials, which exhibit almost no thermal expansion and spontaneous volume magnetostriction. Disordered phases also show the Invar effect in a narrow concentration range and many measurements have been performed on $\text{Fe}_{72}\text{Pt}_{28}$, which has a slightly different composition from Fe_3Pt , because of the martensitic transformation just below room temperature. The anomalous behavior of the thermal coefficient was first reported in Fe-Ni alloys at about 65 to 75 Fe at.% over a century ago [3], but the mechanism behind the effect is still debatable. Weiss proposed that two distinct γ -Fe phases can exist with almost the same energy but different volumes, one ferromagnetic and the other non-magnetic [4]. This phenomenological model has been widely accepted and supported by the band calculations [5], but the real physical origin of the Invar effect may be the electron-phonon interaction in a ferromagnetic metal, suggested by Kim [6].

The Fe-Pt alloys also show complex magnetic behavior [2]. The disordered phases show a ferromagnetic to non-magnetic transition near room temperature, depending

strongly on Fe composition. The Fe magnetic moments in FePt_3 are ordered antiferromagnetically below $T_{N1} = 160$ K, with a high value of local magnetic moment [7]. Even in the ferromagnetic FePt , the ferromagnetic coupling competes with the antiferromagnetic coupling, and FePt is difficult to magnetize [8]. It has been speculated that the magnetic state of Fe alloys in the Invar region may involve collinear arrangements of moments [9,10]; this has not yet been confirmed experimentally in Fe_3Pt .

In order to understand the underlying mechanism of the various interesting properties of the Fe-Pt alloy system, it is important to study the electronic structure of Fe-Pt alloys. Actually, the high-spin to low-spin transition of Fe_3Pt was reported to be confirmed by the observation of the change in the electronic structure by using spin-polarized photoemission spectroscopy [11], but there was some controversy [12]. In this work, we investigated the electronic structure of $\text{Fe}_x\text{Pt}_{1-x}$ ($x = 0.25, 0.5, 0.75$) alloys by using photoemission spectroscopy using synchrotron radiation [13–15]. The Fe $3d$ and Pt $5d$ partial spectral weights (PSWs) were determined by taking advantage of the Cooper minimum phenomenon of Pt $5d$ photoionization cross section, and they are compared with the previous band calculation results.

II. EXPERIMENT

The disordered $\text{Fe}_x\text{Pt}_{1-x}$ alloys ($x = 0.25, 0.50, 0.75$) were made by arc-melting of 99.99 % Fe and 99.9 % Pt in an atmosphere of argon gas. Both metal wires were melted separately before mixing and then melted

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together several times to ensure homogeneity. The face-centered-cubic structure was checked by means of X-ray diffraction, and no other phases were detected. The photoemission spectra of Fe-Pt alloys and of pure metals with synchrotron radiation were taken at beamline 2B1 in Pohang Light Source (PLS). The photon energy we used ranged from 60 eV to 150 eV, and the total experimental resolution was maintained at better than 0.3 eV full width at half maximum. The spectra were measured with a VG CLAM2 analyzer with three channeltron detectors. All measurements were performed at room temperature and under a low pressure of 10^{-10} torr. To remove contaminants, sample surfaces were scraped *in situ* by using a diamond file.

III. RESULTS AND DISCUSSION

Figure 1 represents the photoemission spectra of $\text{Fe}_x\text{Pt}_{1-x}$ alloys and of pure Pt at $h\nu = 120$ eV and 70 eV. The analyzer transmission function which gives the best line shape at binding energies higher than 10 eV was found to be in proportion to $E^{-1.4}$, where E is the kinetic energy of the photoelectrons. For quantitative analysis, inelastic backgrounds were also removed by assuming a step-function-type loss. Because of the binding energy dependence of the matrix elements in the photoionization process, the spectra of pure metals at different photon energies may look quite different. The spectral weight of Pt $5d_{5/2}$ states in pure Pt spectra clearly shows this behavior, which cannot be neglected in the quantitative analysis for extracting the PSWs.

The procedure for extracting the PSWs of binary alloy systems is discussed in detail in Ref. 16. In this procedure, a photoemission spectrum is represented as the sum of contributions from different species of atomic sites, weighted by their photoionization matrix elements, which are dependent both on photon energy and on binding energy. Because of the variation of matrix element with binding energy, the photoemission spectrum or the components from different species are not exactly equal to the total or the partial density of states (DOS) of the alloy system. Therefore, it is necessary to include the matrix elements correctly for extracting the partial spectral weights from the measured photoemission spectra, and for the comparison with calculated partial DOS. If we can determine the matrix elements of the constituents or at least the ratio of the matrix elements between different photon energies, then it is possible to extract the partial spectral weights. Here, we represent the change in matrix elements at two different photon energies by the ratio of the spectra of pure Pt and Fe. It turned out that the Fe spectra at the two photon energies, 70 and 120 eV, did not differ much, and there was negligible matrix-element effect, at least between 70 and 120 eV. However, the Pt spectra differed greatly especially in their relative intensities, between $5d_{3/2}$ and $5d_{5/2}$ states.

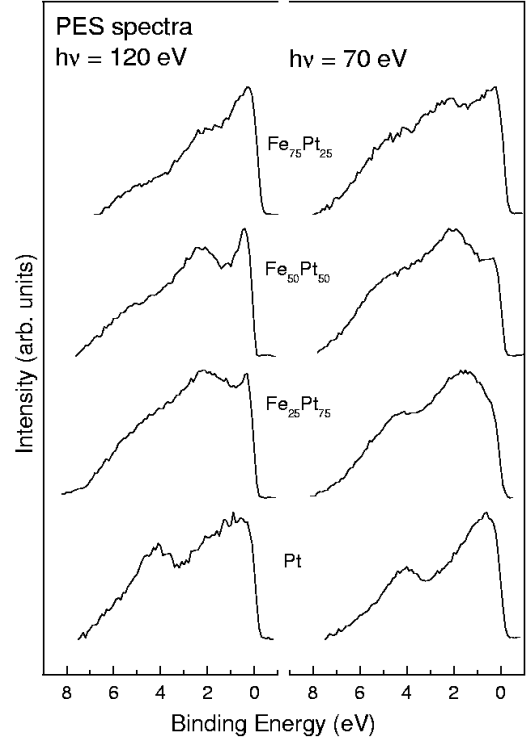


Fig. 1. Photoemission spectra of $\text{Fe}_x\text{Pt}_{1-x}$ alloys and of pure Pt at $h\nu = 120$ eV and 70 eV. The transmission function has been corrected and the inelastic background removed.

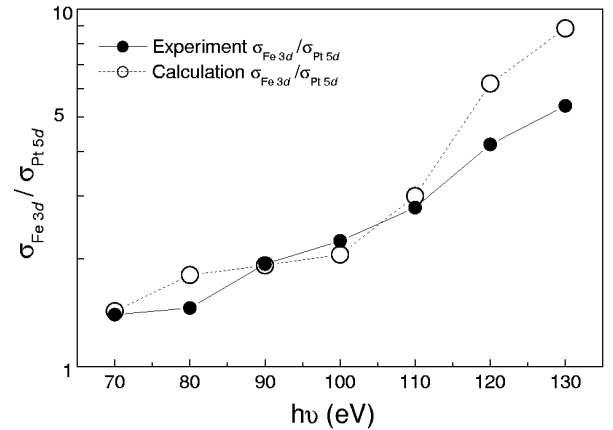


Fig. 2. Photoionization cross-section ratios between Fe 3d and Pt 5d states in the photon energy range of 70–130 eV. The results of the atomic calculation are from Ref. 17.

The experimentally determined ratios between Fe 3d and Pt 5d photoionization cross-section in the photon-energy range of 70 to 130 eV are shown in Figure 2 along with the atomic calculation [17]. Due to the solid-state effect [18], the dip of the cross-section ratio at $h\nu = 100$ eV in the atomic calculation is not very pronounced in the experimental results. Since the experimental value of the cross-section ratio of the Fe 3d to the Pt 5d state is 1.3 at $h\nu = 70$ eV, we can regard the spectrum at

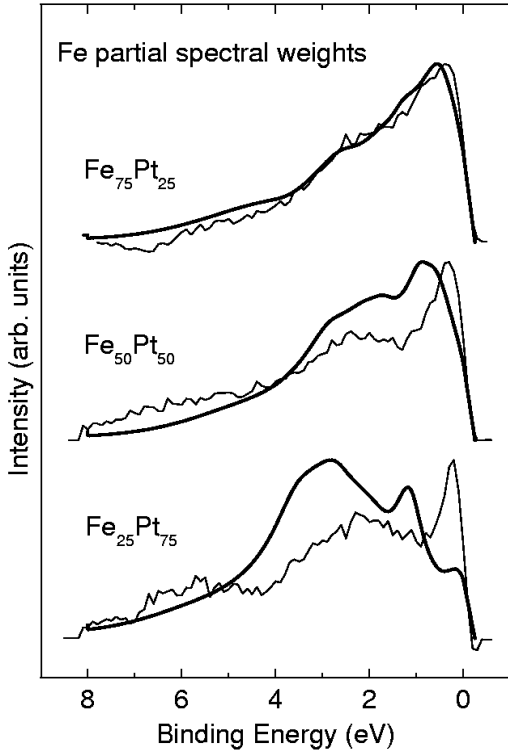


Fig. 3. Fe 3d partial spectral weights of Fe-Pt alloys. Thick lines are theoretical partial spectral weights obtained by using the band-calculation results for ferromagnetic phases in Ref. 19.

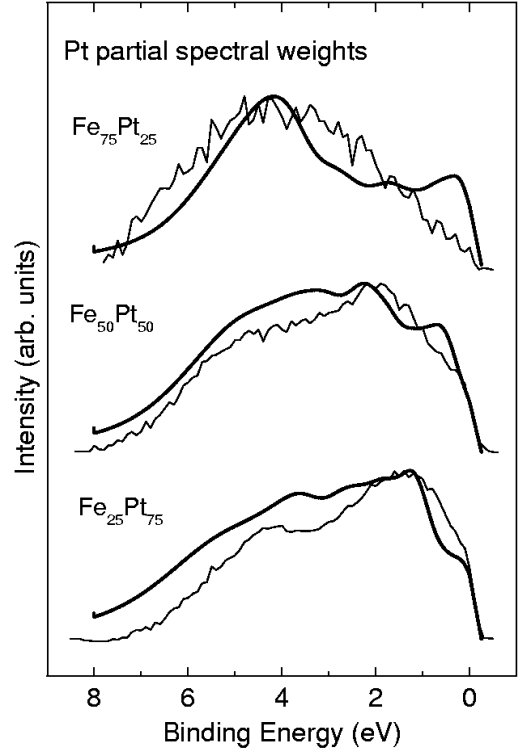


Fig. 4. Pt 5d partial spectral weights of Fe-Pt alloys. Thick lines are theoretical partial spectral weights obtained by using the band-calculation results for ferromagnetic phases in Ref. 19.

that photon energy as the Pt PSW as a first approximation. The spectral ratio used for transforming the Pt PSW at 70 eV into the one at 120 eV is the spectrum of pure Pt at 120 eV divided by that at 70 eV. By using the measured cross-section ratio and the divided spectrum representing the change in the matrix elements of pure Pt between different photon energies, the Fe PSW at 120 eV can be obtained. With this approximate Fe PSW, a better Pt PSW at 70 eV can be determined by a similar method, and the process is iterated until we obtain self-consistent results. In this procedure, we neglect the possible wave-vector dependence of the matrix element. The convergence of the iteration is rather fast, and performing 3 iterations was usually enough.

The results of the analysis are shown in Figures 3 and 4 as thin lines. The real characterization of the electronic structure of Fe-Pt alloys was elucidated by comparison of the experimental results with the theoretical calculation on the ferromagnetic Fe-Pt intermetallics [19]. Since the calculation was scalar-relativistic, the spin-orbit splitting of Pt 5d could not be correctly reproduced. In order to incorporate the lifetime broadening of hole states, we used a binding-energy-dependent lifetime of Fermi liquid by assuming a quadratic form. The theoretical PSWs determined in this way are shown in the figures as thick lines. We neglect binding-energy dependence of the photoionization matrix element, which will reduce the spec-

tral weight at high binding energy [20].

The experimental Pt 5d PSWs are in accord with the theoretical curves, and the band-center of Pt 5d states is lowered with growing Fe concentration, as predicted by the band calculation. However, while the experimental Fe PSW of Fe₇₅Pt₂₅ is very similar to the theoretical curve, that of Fe₂₅Pt₇₅ shows completely different features from the calculation. The pronounced peak at the Fermi level in the experimental Fe PSW, the width of which decreases with Pt content, is absent in the theoretical curve. It may be that the spin splitting of Fe 3d partial DOS of the ferromagnetic FePt₃ does not occur in the paramagnetic disordered Fe₂₅Pt₇₅, and that the spin-down peak at 1.2 eV is not present in the experimental Fe PSW. However, the position of the Fe 3d spin-down peak in Fe₅₀Pt₅₀ does not agree well with the theoretical prediction either, and the discrepancy between the experiment and the band calculation may not be a result of either difference of magnetic phases or neglect of compositional disorder in the calculation. We are currently working on the photoemission spectroscopy of Fe-Pt alloys in their ferromagnetic phases by taking spectra at low temperature in order to find the origin of this discrepancy.

For Fe₇₅Pt₂₅, the underlying mechanism of band formation is band repulsion, which strongly shifts the band-

center of Pt 5d partial DOS. The experimental Pt PSW of Fe₇₅Pt₂₅ is markedly broadened when compared with the theoretical curve, due to the short lifetime caused by compositional disorder [21]. From the figures, it is apparent that the strong mixing between Fe 3d and Pt 5d states occurs in Fe₅₀Pt₅₀. This might enhance the spin-orbit coupling of the Fe 3d electron and explain the good magnetic properties of disordered alloys near the equiatomic concentration.

IV. SUMMARY

In this study, we investigated the electronic structure of Fe_xPt_{1-x} alloys ($x = 0.25, 0.5, 0.75$) by taking valence band spectra with synchrotron radiation. We extracted the partial spectral weights of both constituents by using the Cooper minimum phenomenon of Pt 5d photoionization cross-section and taking the matrix-element effect into consideration. We have shown that the experimental results are similar to the theoretical curves for Fe₇₅Pt₂₅ and Fe₅₀Pt₅₀ alloys. We also observed a marked broadening of the Pt 5d PSW of Fe₇₅Pt₂₅, resulting from disorder. The experimental results for the Fe 3d PSW of paramagnetic Fe₂₅Pt₇₅ were very different from the calculation on the ferromagnetic phase FePt₃, probably due to the absence of band splitting in the paramagnetic phase.

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