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# Electron spectroscopic evidence of electron correlation in Ni–Pt alloys: comparison with specific heat measurement

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Received 7 November 2002, in final form 12 March 2003

Published 6 May 2003

Online at [stacks.iop.org/JPhysCM/15/3191](http://stacks.iop.org/JPhysCM/15/3191)

## Abstract

We have performed photoemission spectroscopy of Ni–Pt alloys to understand the origin of the discrepancy between the experimental linear coefficient of specific heat  $\gamma$  and that predicted by band theory. We found that the quasiparticle density of states at the Fermi level deduced from photoemission measurement is in agreement with the experimental value of  $\gamma$ , if we include the electron correlation effect. It was also found that the Ni 2p core level satellite intensity increases as Ni content is reduced, indicating a strong electron correlation effect which can enhance the quasiparticle effective mass considerably. This supports our conclusion that electron correlation is the most probable reason of disagreement of  $\gamma$  between experiment and band theory.

## 1. Introduction

Within the one-electron band theory of solids, the linear coefficient of specific heat  $\gamma$  is proportional to the electron density of states at the Fermi level  $N(E_F)$  [1]. However, when electron–electron interaction is introduced, the effective mass  $m^*$  of the quasiparticle is changed [2] and this will affect the quasiparticle DOS at the Fermi level  $N^*(E_F)$  and, as a result,  $\gamma$ . This effect has been observed for many systems including transition metals and their compounds. For Ni, Co and Fe, it has been found that the discrepancy in  $\gamma$  values between the local-density approximation (LDA) calculation and the experiment can be removed by taking the on-site Coulomb interaction into account [3].

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Ni is one of the most remarkable cases in that strong on-site Coulomb repulsion results in the two-hole satellite in photoemission spectrum along with the enhancement of  $N^*(E_F)$ . Core levels also have satellites due to the Coulomb interaction between core holes and valence electrons [4] and its presence and energy positions have been studied in detail [5]. These effects are expected to be enhanced when the on-site Coulomb interaction  $U$  is large and the bandwidth  $W$  is small. For transition metal compound  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ , the strong deviation of the spectral weight near the Fermi level from a LDA calculation and that of  $\gamma$  values was interpreted as a result of strong  $k$  dependence of the quasiparticle self-energy which modifies  $m^*$  significantly [6].

For disordered alloys, the comparison of measured  $\gamma$  values and theoretically predicted  $N(E_F)$  had not been studied carefully until the Korringa–Kohn–Rostocker coherent potential approximation (KKR-CPA) method was developed as a reliable calculation scheme which can handle the randomness of the potential at an atomic site [7, 8]. Among various alloys studied so far, Ni–Pt alloy has been one of the most striking examples showing large deviation of calculated values  $\gamma^{\text{cal}}$  from the measured one  $\gamma^{\text{exp}}$ .  $\text{Ni}_x\text{Pt}_{1-x}$  is famous for its magnetic transition from the paramagnetic to ferromagnetic phase as the Ni concentration becomes larger than 0.4 [9]. Experimentally, calorimetric measurements showed a large increase of  $\gamma^{\text{exp}}$  near the magnetic transition composition, but the electronic structure of  $\text{Ni}_x\text{Pt}_{1-x}$  alloys calculated with the non-self-consistent field (non-SCF) relativistic KKR-CPA method [10] showed no such enhancement in theoretical  $\gamma^{\text{cal}}$  at all. More recent SCF non-relativistic calculations [11] on  $\text{Ni}_{50}\text{Pt}_{50}$  could not explain the experimentally observed huge increase of  $\gamma^{\text{exp}}$ , which is more than twice the calculated value. Also it was pointed out in [10] that neither paramagnon nor electron–phonon interactions can explain this discrepancy.

Except for the aforementioned striking disagreement of  $\gamma$  values between theory and experiment, physical properties of the Ni–Pt alloy system are relatively well understood thanks to extensive studies on its magnetic properties and the phase diagram. Neutron scattering study [12, 13] showed that in the ferromagnetic phase the Pt site of Pt-diluted alloys also has a sizeable magnetic moment probably because of hybridization between Pt and Ni d-electron wavefunctions near  $E_F$  [14]. The average magnetic moment is decreased as the Pt concentration increases, and vanishes at about 60 at.% of Pt. The Curie temperature has a different concentration dependence for ordered and disordered alloys, making disordered  $\text{Ni}_{50}\text{Pt}_{50}$  ferromagnetic below 150 K while ordered NiPt is paramagnetic.

The electronic structure of Ni–Pt alloys is also relatively well understood. The charge transfer between Ni 3d and Pt 5d states was discussed using core level photoemission spectroscopy (PES) [15, 16] and it was concluded that both intra-atomic and inter-atomic charge transfer are important in alloys [16]. The valence band partial spectral weight was studied using the Cooper minimum phenomenon [17] and it was shown that the bandwidth  $W$  of Ni 3d states at  $E_F$  becomes smaller as the Ni concentration is decreased and that there remains appreciable Pt 5d spectral weight at  $E_F$  even for 10% Pt alloy.

In this paper, we report ultraviolet photoemission spectroscopy (UPS) results on Ni–Pt alloys to understand the origin of the huge enhancement of  $\gamma$  near the magnetic transition composition. Since the strong correlation effect in metallic systems usually results in the enhancement of  $m^*$ , the increase of  $N^*(E_F)$  is expected to be driven by the electron correlation as in Ni [3]. In principle, if we can determine the Ni 3d wavefunction renormalization factor  $Z_{\text{Ni}}$  for all the compositions, we can deduce  $N^*(E_F)$  from the calculated values of Ni and Pt partial DOS at  $E_F$ . However, it may be possible that part of the discrepancy of  $\gamma$ , if not all, results from the error in band calculation, especially for Ni 3d partial DOS which has a sharp feature at  $E_F$ . We extract  $N^*(E_F)$  by determining  $Z_{\text{Ni}}$  values from the core level x-ray photoemission spectroscopy (XPS) and by using the valence band spectra and the calculated Pt

partial DOS. The satellite intensity of the Ni 2p core level increases as Ni content is decreased, which implies a stronger correlation effect of the valence band. We assumed that the relative core level satellite intensity is proportional to its valence band counterpart.

The values of  $\gamma$  determined in this way were found to be in good agreement with the existing calorimetric measurements [18, 19]. From the results in this paper, we argue that the anomalous increase of  $\gamma$  near magnetic transition composition originates mainly from electron correlation of Ni 3d electron states at  $E_F$ . It is also probable that the band calculation results underestimate Ni partial DOS at  $E_F$ .

This paper is organized as follows. The experimental details are described in section 2. In section 3, the high resolution photoemission spectra of valence bands and the Ni 2p XPS core level spectra are presented. In section 4, we extract the experimental  $N^*(E_F)$  values of Ni and  $\text{Ni}_x\text{Pt}_{1-x}$  alloys ( $x = 0.10, 0.30, \text{ and } 0.50$ ) for comparison with the existing experimental  $\gamma$  values and with those predicted by band theory. Finally, concluding remarks are added in section 5.

## 2. Experimental details

Polycrystalline disordered  $\text{Ni}_x\text{Pt}_{1-x}$  alloys with  $x = 0.10, 0.30$  and  $0.50$  were made by melting appropriate amounts of constituent elemental metals in an arc furnace under an inert argon atmosphere. The melted buttons were separately sealed in an evacuated quartz ampoule and annealed at  $1200^\circ\text{C}$  for a day to ensure homogeneity. The structure was checked with x-ray diffraction.

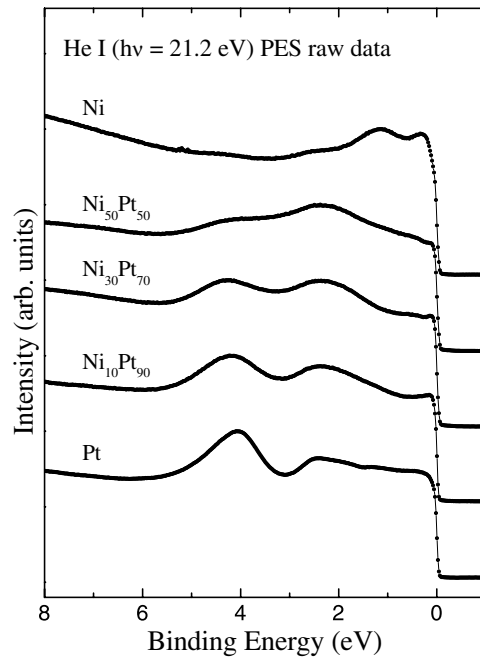
The valence-band PES data were taken with a VG Microtech CLAM 4 multi-channeltron detector electron energy analyser with resolution of 30 meV in half-width at half-maximum (HWHM) and the base pressure was  $1.5 \times 10^{-10}$  Torr. The photon source was unmonochromatized He I lines ( $h\nu = 21.2$  eV). The samples were cooled down to 95 K with liquid nitrogen and the surfaces were scraped *in situ* at that temperature until clean spectra free of oxygen contamination were obtained. Since the photon energy was well away from the Ni  $3p \rightarrow 3d$  resonance, the two-hole satellite of Ni could hardly be observed in the UPS spectra.

XPS spectra were taken with unmonochromatized Al  $K\alpha$  lines ( $h\nu = 1486.6$  eV). The photocurrent measurement was performed with a VSW Scientific Instruments HA150 concentric hemispherical analyser. The total instrumental resolution was 0.5 eV in HWHM. The base pressure was kept better than  $5 \times 10^{-10}$  Torr and measurements were done at room temperature. In order to remove contaminants on the surface, the samples were either scraped or sputtered with 2.0 keV argon ions for more than 30 min and the cleanliness of the sample surface was checked by monitoring C 1s and O 1s core levels. Since sputtering preferentially removes Pt [20], the surface was slightly enriched in Ni, but there was little difference in core-level lineshape between sputtered and scraped surfaces.

## 3. Photoemission results

### 3.1. Valence band spectra

Figure 1 shows the spectra of pure Ni, Pt and  $\text{Ni}_x\text{Pt}_{1-x}$  alloys ( $x = 0.10, 0.30$  and  $0.50$ ) at 95 K with  $h\nu = 21.2$  eV. Fine structure around the Fermi level is visible in each spectrum; the splitting of the majority and minority spin states of ferromagnetic Ni, decrease of spectral weight of Pt near  $E_F$  predicted by band calculations [21, 22] and sharp peaks at  $E_F$  for paramagnetic Ni–Pt alloys ( $x = 0.10$  and  $0.30$ ). It seems that, due to a strong photoemission matrix element effect, the spectral weight with binding energy  $E_B > 6$  eV is almost absent in this UPS spectra although the band calculation predicts that the bottom of the Pt d band extends



**Figure 1.** Photoemission raw spectra of Ni, Ni<sub>x</sub>Pt<sub>1-x</sub> ( $x = 0.10, 0.30$  and  $0.50$ ) and Pt with  $h\nu = 21.2$  eV at 95 K.

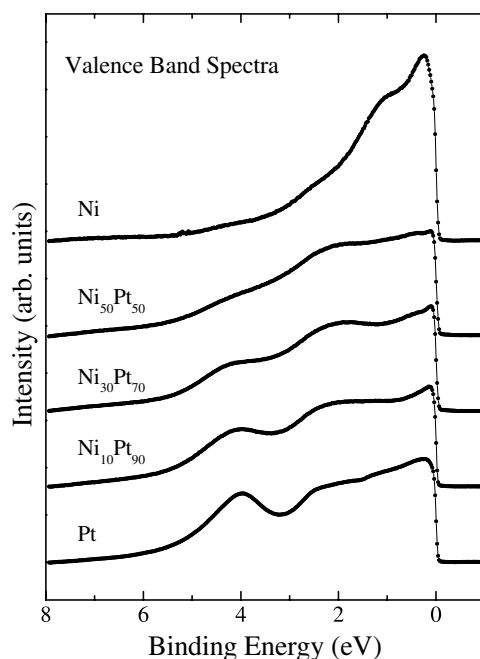
to  $E_B = 7.2$  eV and the XPS spectrum shows an appreciable amount of spectral weight even at  $E_B > 10$  eV [15]. Similar behaviour has been observed for Cu–Pd alloys [23]. The Ni spectrum has little spectral weight attributable to the two-hole satellite at this photon energy.

The absence of satellite spectral weight in fact makes it possible to determine  $N^*(E_F)$  from the  $k$  integrated photoemission spectra. According to the normal Fermi liquid theory, the spectral weight at the Fermi energy  $\rho(E_F)$ , which is measured by photoemission, is the same as the non-interacting electron DOS [24]:

$$\rho(E_F) = ZN^*(E_F) = N(E_F), \quad (1)$$

when the electron–electron interaction is represented by the local self-energy which does not have  $k$  dependence. Here  $Z$  is the wavefunction renormalization factor, which also makes the quasiparticle bandwidth decrease from the non-interacting value  $W$  to  $ZW$ . This implies that, while the quasiparticle DOS at  $E_F$  is enhanced as  $N^*(E_F) = N(E_F)/Z$ , the spectral weight of the coherent part is normalized by a factor of  $Z$ . The remaining  $1 - Z$  of the spectral weight is transferred to the incoherent part of the spectral function. Hence if we know the value of the renormalization factor  $Z$ , we can determine the quasiparticle DOS  $N^*(E_F)$  from the measured spectral weight  $\rho(E_F)$  by calculating  $\rho(E_F)/Z$ .

For quantitative analysis based on area normalization of PES spectra, the analyser transmission function and inelastic background should be corrected and removed. The transmission function is generally approximated as  $1/E$  where  $E$  denotes the kinetic energy of an outgoing photoemitted electron. After correction, the intensity of Ni spectra at  $E_B > 6$  eV almost vanished, indicating that  $1/E$  correction is adequate for our analyser. The inelastic background was removed, assuming that the electron energy loss function can be approximated as a step function. The relative weight of the background contribution is determined iteratively by fitting. The result of transmission function correction and background removal is shown



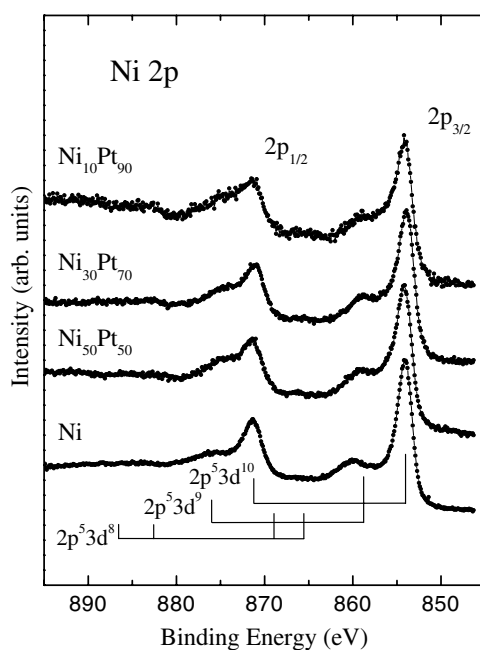
**Figure 2.** Corrected valence band photoemission spectra of figure 1. The analyser transmission function was assumed to be proportional to the inverse of photoelectron kinetic energy. The inelastic background has also been removed.

in figure 2. The overall structure is more clearly visible than in the raw spectra. The binding energies of the peaks near  $E_F$  are 0.23 and 0.17 eV for Ni and Pt, respectively, while those of alloys are 0.11 eV, which means that the peak of the quasiparticle DOS is at or very close to  $E_F$  for paramagnetic Ni–Pt alloys. This sharp feature at  $E_F$ , which is not present either in Ni or in Pt spectra, must be related to the huge enhancement of  $\gamma$  at magnetic transition composition.

### 3.2. Core level spectra

The satellite feature in photoemission spectra of Ni has attracted great interest since its discovery [25] and much theoretical effort has been done to understand its origin [5, 26]. The underlying physics is that the ground state of Ni contains a  $d^9$  configuration as well as a  $d^{10}$  and when a d electron is removed by photoemission, there can be two holes in the valence band in the final state which are localized at an atomic site. Experiencing strong on-site Coulomb interaction, these two holes form a bound state as a satellite in photoemission spectra which can be well described with the first-principle calculation [27].

For core levels, the origin of satellites is the same as that of the valence band, and its relation to the valence electronic structure was systematically studied over various Ni alloys [28, 29]. The relation between the valence Ni 3d partial DOS and the core level satellite intensity was that if the quasiparticle DOS at  $E_F$  increases as a result of band narrowing so does the relative intensity of satellites. This satellite is diminished when valence states with mostly d character are occupied, leaving some d states as unoccupied which are strongly hybridized with s and p electrons. This means that if a core satellite is present, there can be enhancement of  $m^*$  as a result of correlation. Most alloy systems studied in [28] and [29] have smaller or even vanishingly small Ni partial DOS of mostly d character at  $E_F$ , which reduces the satellite



**Figure 3.** Ni 2p core level spectra with  $h\nu = 1486.6$  eV at room temperature. The positions of atomic configurations corresponding to the main peak and satellites are approximately shown at the bottom of the figure. Note the increase of satellite intensity as Ni is diluted.

intensity, but when the enhancement of partial  $N(E_F)$  is expected, one can see larger relative satellite intensity.

In order to see whether there really is some enhancement of the electron correlation effect of Ni upon alloying with Pt, we performed an XPS experiment and the Ni 2p spectra of pure Ni and Ni–Pt alloys from sputtered surfaces are presented in figure 3. Approximate positions of different atomic configurations are shown at the bottom of the figure following [30]. It is apparent that the satellite structure with higher binding energy by about 4.6 eV than the Ni 2p<sub>3/2</sub> main line, which corresponds to the configuration of 2p<sup>5</sup>3d<sup>9</sup>, gains more weight relative to the main peak as Ni is diluted. Also another broad satellite with binding energies higher than the main line by 14.4 eV corresponding to the configuration of 2p<sup>5</sup>3d<sup>8</sup> becomes prominent as Ni content is reduced. These indicate that, although we do not know the exact partial DOS at  $E_F$ , we can qualitatively argue that the correlation effect becomes stronger as Ni content is decreased.

In fact, for a narrow band system, the relative core level satellite intensity was suggested as [31]

$$\frac{I(d_9)}{I(d_{10})} = \frac{n_h - cW/Q}{1 - n_h + cW/Q}, \quad (2)$$

where  $I(d_9)$  and  $I(d_{10})$  are the core level photoemission intensity of the first satellite structure and the main peak of Ni, respectively,  $Q$  is the Coulomb interaction between the core hole and the valence electron and  $c$  is a constant depending on band filling and band degeneracy. From the above equation, one can argue that the enhancement of the relative intensity of satellite structure is solely due to the change in the number of holes in the d band,  $n_h$ . However, a systematic study on charge transfer in Ni–Pt alloys [16] showed that the amount of charge

**Table 1.** Relative main peak intensities of the Ni 2p core level spectra and the values of  $Z_{\text{Ni}}$  of  $\text{Ni}_x\text{Pt}_{1-x}$  alloys ( $x = 0.10, 0.30, 0.50$  and  $1.00$ ).

	$I_0/I_{\text{tot}}$	$Z_{\text{Ni}}$
Ni	$0.68 \pm 0.01$	0.74
$\text{Ni}_{50}\text{Pt}_{50}$	$0.57 \pm 0.02$	0.62
$\text{Ni}_{30}\text{Pt}_{70}$	$0.54 \pm 0.02$	0.59
$\text{Ni}_{10}\text{Pt}_{90}$	$0.51 \pm 0.02$	0.55

transferred from the Ni d band is at most 0.03 electrons, even for the Ni 10% case, and the observed increase in the satellite intensity of Ni 2p core levels upon alloying can be attributed to stronger electron correlation in alloys.

For quantitative analysis, the intensity ratios of  $2p^53d^9$  and  $2p^53d^8$  satellites relative to the whole Ni  $2p_{3/2}$  intensity were determined. The Ni  $2p_{3/2}$  peaks were fitted assuming the same lineshape throughout the whole composition range for the main peak whose atomic configuration is  $2p^53d^{10}$  and using composite peaks to fit the  $2p^53d^9$  satellite. The  $2p^53d^8$  satellite was fitted with a broad peak although its shape is very complex composed of many multiplets. The approximate error of this fitting procedure is estimated to be  $\pm 5\%$  for the ratio  $I_1/I_0$  between the  $2p^53d^9$  satellite intensity  $I_1$  and that of the main line  $I_0$  and  $\pm 10\%$  for the ratio  $I_2/I_0$  between the  $2p^53d^8$  satellite intensity  $I_2$  and  $I_0$ .

For pure Ni,  $I_1/(I_0 + I_1)$  was found to be 0.31 which is in good agreement with 0.29 in [28] and the value for  $\text{Ni}_{50}\text{Pt}_{50}$  was 0.40. When the second satellite was included, the ratio of total satellite intensity relative to the total Ni  $2p_{3/2}$  intensity  $(I_1 + I_2)/I_{\text{tot}}$  increases from 0.32 for pure Ni to 0.49 for  $\text{Ni}_{10}\text{Pt}_{90}$ . This overall trend is almost the same as in Ni–Pd alloys [32]. The relative main peak intensities  $I_0/I_{\text{tot}}$  are listed in table 1.

#### 4. Relation with the linear coefficient of specific heat

The linear coefficient of specific heat  $\gamma$  is proportional to the quasiparticle DOS at  $E_F$  as

$$\gamma = \frac{1}{3}\pi^2 k_B^2 N^*(E_F) \quad (3)$$

and, in principle,  $N^*(E_F)$  is what we need to know. When the local approximation holds [33], the photoemission spectrum of a binary alloy can be represented as

$$I(E) = \sum_{\alpha} x_{\alpha} \sigma_{\alpha}(E) \rho_{\alpha}(E) \quad (4)$$

where  $x_{\alpha}$  is the concentration of a constituent atom  $\alpha$ ,  $\sigma_{\alpha}(E)$  is the photoionization matrix element of the valence d states of the constituent  $\alpha$ , generally referred to as the photoionization cross section in atomic view, and  $\rho_{\alpha}(E)$  is the spectral weight of the constituent atom  $\alpha$ . The local approximation holds for photon energies as low as 40 eV, but it is generally assumed to hold even for 20 eV, because the valence-band spectra of pure metals taken with He I lines are, in general, similar to those taken with higher photon energies [34]. Here we will consider contributions from Ni 3d and Pt 5d electrons only, since other valence electrons such as s and p levels have negligible cross section. In this equation, both  $I(E)$  and  $\rho_{\alpha}(E)$  are concentration-dependent. The normalization condition is such that

$$\begin{aligned} \int dE I(E) &= \sum_{\alpha} x_{\alpha} \sigma_{\alpha}(E) \int dE \rho_{\alpha}(E) \\ &\simeq \sum_{\alpha} x_{\alpha} \sigma_{\alpha} n_{\alpha} \end{aligned} \quad (5)$$

where  $n_{\alpha}$  is the number of occupied d electrons of the constituent atom  $\alpha$ .



Since the photoemission spectrum is composed not only of the coherent part which represents the quasiparticle band, but also of the incoherent part which usually shows up as electron-correlation-driven satellites, the direct extraction of  $N^*(E_F)$  from photoemission spectrum is complicated. However, as shown in figure 2, none of the spectra of pure Ni, Pt and Ni–Pt alloys have spectral weights attributable to the satellites, possibly due to the negligible cross section at this low photon energy. Hence we can conclude that PES spectral functions in figure 2 effectively represent only the coherent part, not the whole spectral function  $\rho(E)$ . Then equation (4) can be modified as

$$\begin{aligned} I(E) &= \sum_{\alpha} x_{\alpha} \sigma_{\alpha}(E) \left[ \sum_{\mathbf{k}} A(\mathbf{k}, E) \right] \\ &\simeq \sum_{\alpha} x_{\alpha} \sigma_{\alpha}(E) Z_{\alpha} \left[ \sum_{\mathbf{k}} Z_{\alpha, \mathbf{k}}(E)^{-1} A(\mathbf{k}, E) \right] \\ &= \sum_{\alpha} x_{\alpha} \sigma_{\alpha}(E) Z_{\alpha} N_{\alpha}^*(E), \end{aligned} \quad (6)$$

where  $A(\mathbf{k}, E)$  is the coherent part spectral function and  $Z_{\alpha, \mathbf{k}}(E)$  is the renormalization factor of the partial quasiparticle band of a constituent atom  $\alpha$ .  $Z_{\alpha}$  is the renormalization factor in an average sense which reflects the fraction of the total spectral intensity showing up as coherent states, when we assume that  $Z$  is independent of  $\mathbf{k}$ .

The normalization condition in this case can be defined by

$$\begin{aligned} \int dE I(E) &= \sum_{\alpha} x_{\alpha} \sigma_{\alpha}(E) \int dE Z_{\alpha} N_{\alpha}^*(E) \\ &\simeq \sum_{\alpha} x_{\alpha} \sigma_{\alpha} Z_{\alpha} n_{\alpha}. \end{aligned} \quad (7)$$

Since the states with predominantly d character are almost filled both for Ni and Pt, and since there is little change in this number for alloys [16], we can also approximate  $n_{\alpha}$  in equation (6) as a constant.

Then, regardless of their absolute values, the spectra in figure 2 can be normalized using  $\sigma_{\alpha} Z_{\alpha}$  weighted values. For Pt 5d states, we will fix  $Z_{\text{Pt}} = 1$  for the whole compositions, because the correlation effect is expected to be much smaller than in Ni. From equations (6) and (7), if  $N_{\text{Pt}}(E_F)$  and  $Z_{\text{Ni}}$  are known,  $N_{\text{Ni}}^*(E_F)$  and  $N^*(E_F)$  can be determined by the following equations:

$$\begin{aligned} N_{\text{Ni}}^*(E_F) &= \frac{I(E_F)}{x_{\text{Ni}} \sigma_{\text{Ni}} Z_{\text{Ni}}} - \frac{(1 - x_{\text{Ni}}) \sigma_{\text{Pt}}}{x_{\text{Ni}} \sigma_{\text{Ni}} Z_{\text{Ni}}} N_{\text{Pt}}(E_F) \\ &= \frac{N_{\text{Ni}}(E_F)}{Z_{\text{Ni}}}, \end{aligned} \quad (8)$$

$$N^*(E_F) = x_{\text{Ni}} N_{\text{Ni}}^*(E_F) + (1 - x_{\text{Ni}}) N_{\text{Pt}}^*(E_F). \quad (9)$$

Using equations (3) and (9), one can in principle determine the values of the quasiparticle DOS at a Fermi level  $N^*(E_F)$  and of the linear coefficient of specific heat  $\gamma$ . Here, since the slight difference in the Fermi level position in band calculation may cause drastic changes in the Ni partial DOS at the Fermi level  $N_{\text{Ni}}(E_F)$  due to its sharp feature near the  $E_F$ , we only used the calculated values of the Pt partial DOS at the Fermi level  $N_{\text{Pt}}(E_F)$  leaving  $N_{\text{Ni}}(E_F)$  as unknown.

The renormalization factor  $Z$  of pure metals can be estimated in principle by measuring the spectral intensity ratio between the satellite structure and the quasiparticle band, or by comparing the experimental thermal electron mass to the theoretical value, if  $Z$  can be assumed

to be independent of  $k$  and  $\omega$ . For Ni, it is well known that the electron correlation causes the enhancement of thermal electron mass by a factor of 1.35 [3], which can be regarded as the inverse of  $Z_{\text{Ni}}$ . Then the quasiparticle bandwidth is expected to be 74% of the bare electron bandwidth, which is in good agreement with the experimentally observed [35] and calculated [5] quasiparticle bandwidth, which is 25% smaller than the band calculation. This implies that, at least for Ni,  $Z_k(E)$  can be considered as constant and  $Z_{\text{Ni}}$  in equation (6) is the same as  $Z(E_F)$ .

The determination of  $Z_{\text{Ni}}$  is impossible from the UPS valence band spectra due to the negligible contribution of satellite structure for  $h\nu = 21.2$  eV, and even the XPS valence band spectra cannot be used for this purpose because the satellites overlap with the Pt partial spectral weights. Here we instead assume a simple relation

$$Z_{\text{Ni}} = \frac{I_{3d}(\text{main})}{I_{3d}(\text{tot})} \propto \frac{I_{2p}(\text{main})}{I_{2p}(\text{tot})}, \quad (10)$$

where  $I_{3d}(\text{main})$  and  $I_{3d}(\text{tot})$  are the coherent part and the total intensities of the Ni 3d partial spectral weight. Actually, the general rule about the valence band satellite intensity is that it increases as the Coulomb repulsion  $U$  increases relative to the bandwidth  $W$  for fixed hole concentration [36], which is qualitatively in accord with equation (2), the relation for the relative core level satellite intensity.

Then equation (10) can be used to determine the renormalization factors in alloys by the relation

$$Z_{\text{Ni}}(\text{alloy}) = \frac{[I_{2p}(\text{main})/I_{2p}(\text{tot})]_{\text{alloy}}}{[I_{2p}(\text{main})/I_{2p}(\text{tot})]_{\text{Ni}}} Z_{\text{Ni}}(\text{Ni}). \quad (11)$$

The values of  $Z_{\text{Ni}}$  are listed in table 1, using  $Z_{\text{Ni}}(\text{Ni}) = 1.35^{-1}$  [3].

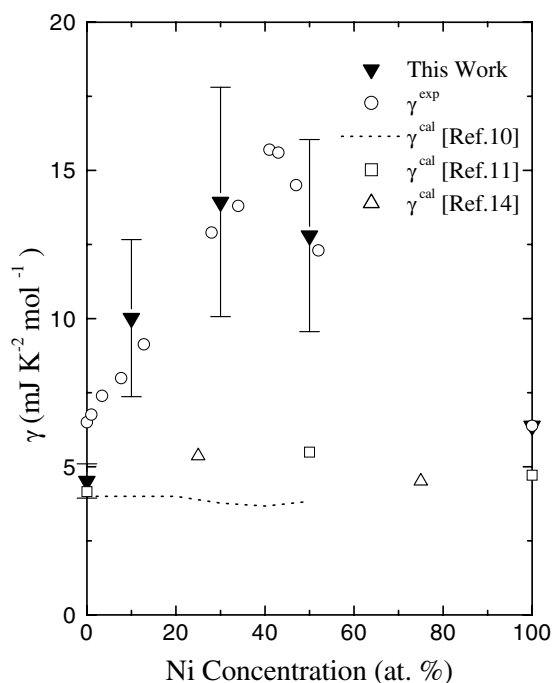
For the photoionization cross section  $\sigma$ , we used an experimentally determined ratio between Ni 3d and Pt 5d states of pure Ni and Pt, respectively. Since the atomic values are expected to be applicable to core levels even in a solid, this ratio can be related to their core level counterpart between Ni 2p and Pt 4f taken with  $h\nu = 1486.6$  eV and to the PES intensity ratios of valence bands and of core levels by

$$\frac{\sigma_{\text{Ni } 3d}}{\sigma_{\text{Pt } 5d}} = \frac{Z_{\text{Pt}}}{Z_{\text{Ni}}} \frac{I_{\text{Ni valence}}/I_{\text{Ni } 2p}}{I_{\text{Pt valence}}/I_{\text{Pt } 4f}} \frac{\sigma_{\text{Ni } 2p}}{\sigma_{\text{Pt } 4f}} \quad (12)$$

if the measurements are performed under the same conditions. Here we take into account the fact that the spectra in figure 2 taken with  $h\nu = 21.2$  eV are devoid of satellite structures which correspond to the incoherent part of the spectral weight. The experimental value thus determined is 0.21, 52% larger than the theoretical one [37].

Finally, for the determination of  $\gamma$ , we need to know  $N_{\text{Pt}}(E_F)$  in equation (9). In this work, we used linear interpolation of the calculated values of a Pt partial electron DOS at the Fermi energy  $N_{\text{Pt}}(E_F)$  for pure Pt [21] and Ni<sub>50</sub>Pt<sub>50</sub> [11], 24 and 14.5 states/(Ryd atoms), respectively.

The result of simple calculation for  $\gamma$  using equation (9) is shown in figure 5 as solid triangles. The open circles in the figure are the calorimetric measurements  $\gamma^{\text{exp}}$  [18, 19]. The band calculation results are plotted as squares for Pt, Ni and Ni<sub>50</sub>Pt<sub>50</sub> [11], as a broken line for paramagnetic Pt-rich alloys [10], and as open triangles for ordered phases NiPt<sub>3</sub> and Ni<sub>3</sub>Pt [14]. The values of this work are normalized to have the value of  $\gamma^{\text{exp}}$  for Ni. It is very surprising in that the agreement between calorimetric measurement and this work is almost perfect, but this is largely because some factors are related and the errors from those factors cancel each other somewhat. The present results should not be interpreted as saying that the quantitative agreement is really perfect.



**Figure 4.** Linear coefficient of specific heat of Ni–Pt alloys. The full triangles are from the present determination of  $N^*(E_F)$  from equations (3) and (10) with error bars, open circles are the calorimetric measurement in [18, 19] and the broken line, squares and open triangles are from various band calculations in [10, 11, 14]. The values in this work are normalized to have the same  $\gamma$  value for pure Ni as the calorimetric value, which is the circle overlapped with the solid triangle on the left ordinate.

Factors contributing to errors were normalization of the spectra, transmission function correction, background removal, using the experimental value of  $\sigma$  ratio, using the theoretical  $N_{Pt}(E_F)$  of  $Ni_{50}Pt_{50}$  and the estimation of  $Z_{Ni}$  of alloys in equation (11). When we took these factors into consideration, error bars could be marked as in figure 4.

## 5. Discussion

In principle, if the previous band calculation results are correct, we can determine  $N^*(E_F)$  and  $\gamma^{cal}$  values using theoretical  $N_{Ni}(E_F)$  and  $N_{Pt}(E_F)$  along with the averaged normalization factors  $Z_{Ni}$  in table 1. However, this can remove only about one-third of the discrepancy between  $\gamma^{cal}$  and  $\gamma^{exp}$  shown in figure 4. This implies either that the electron correlation effect in the valence band is underestimated or that the band calculation underestimates  $N(E_F)$  of alloys. In fact,  $N_{Ni}(E_F)$  of  $Ni_{50}Pt_{50}$  extracted using equation (8) has a larger value than the CPA calculation in [11] by 74%. The reason for this discrepancy may be the unavailability of the fully relativistic self-consistent-field calculation. However, as we have briefly discussed in section 1 and shown in figure 4, the disagreement between LDA and the specific heat coefficient measurement is so large that an enhanced electron correlation effect is expected in these alloys which increases the effective mass and thereby  $\gamma$ .

In figure 5, we reproduced Ni partial spectral weights shown in figure 5 of [17] to support the conclusion that the electron correlation effect is stronger in alloys than in pure Ni metal.

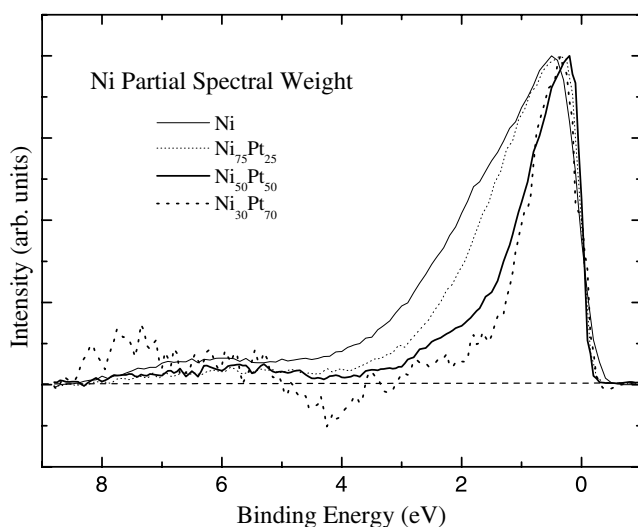


Figure 5. Ni 3d partial spectral weights of Ni, Ni<sub>75</sub>Pt<sub>25</sub>, Ni<sub>50</sub>Pt<sub>50</sub> and Ni<sub>30</sub>Pt<sub>70</sub> (from [17]).

As Ni is diluted, the bandwidth is reduced from its value of pure Ni by about 50% even in Ni<sub>50</sub>Pt<sub>50</sub>. The absence of spectral intensity at  $E_B > 4$  eV must result from very low  $\sigma$  values at higher binding energy as discussed before. Then, even if the on-site Coulomb interaction  $U$  is the same,  $U/W$  will be increased, and as a result, further enhancement of  $N^*(E_F)$  relative to the LDA calculation will occur due to a stronger correlation effect than in pure Ni. Hence the most probable reason of the disagreement between the CPA calculation and experiments will be the electron correlation of electron states at  $E_F$  which can greatly modify  $m^*$ .

## 6. Conclusion

In this work, we have shown that the quasiparticle DOS at  $E_F$  of Ni–Pt alloys, which is proportional to the linear coefficient of specific heat  $\gamma$ , obtained from photoemission spectroscopy is in agreement with the previous calorimetric studies.

The disagreement between  $\gamma^{\text{cal}}$  values predicted by theoretical band calculation and the experimentally measured  $\gamma^{\text{exp}}$  could be qualitatively understood with the introduction of an electron correlation effect, which enhances the quasiparticle DOS at  $E_F$  as the width of the band at  $E_F$  becomes smaller.

In order to see the correlation effect of the valence band at  $E_F$  indirectly, we have performed Ni 2p core level photoemission spectroscopy. As the Ni content was reduced, the satellite intensity grew, which implies the enhanced correlation effect of electron states at  $E_F$ , since the number of d electrons does not change much [16].

The previous study on Ni partial spectral weights [17] shows that, as Ni is diluted, the band at  $E_F$  becomes narrow and, as a result, experiences a stronger correlation effect due to the increased  $U/W$  value, which enhances the quasiparticle effective mass of the alloy with equiatomic composition much greater than that of Ni. This ensures that the underlying mechanism of the huge enhancement of the effective mass in Ni–Pt alloy is the electron correlation of mostly Ni 3d character band which crosses the Fermi level.

Finally, the present explanation of the discrepancy between  $\gamma^{\text{cal}}$  and  $\gamma^{\text{exp}}$  we believe is also applicable to the similar results observed in Ni–Pd and Ni–Cu alloys [38, 39].

## Acknowledgments

The work in Seoul National University was supported by Science Research Center Program of Korea Science and Engineering Foundation (KOSEF) through Center for Strongly Correlated Materials Research. T-UN also wishes to thank Dr Seung-Ho Lee for finding useful references.

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