

Unoccupied States and the Charge Transfer in Cu-Pt Alloys Studied by Bremsstrahlung Isochromat Spectroscopy and X-ray Photoelectron Spectroscopy

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We have measured the unoccupied partial Pt 5*d* densities of states in Cu-Pt alloys by using bremsstrahlung isochromat spectroscopy (BIS). We found that the Pt 5*d* states are gradually filled up as the Pt concentration is reduced. We have also determined the charge redistribution between the Pt and the Cu atoms from the core-level binding-energy shifts in the X-ray photoelectron spectroscopy (XPS) and the intensity of the unoccupied Pt *d* states in the BIS spectra. We found that inter-atomic charge transfer is generally small and that intra-atomic charge redistribution between *s* and *d* electrons is more important for the change of electronic structures in alloys.

I. INTRODUCTION

Alloy systems have attracted much attention lately because of both their interesting physical properties and their potential technological applications, such as invar alloys, shape memory alloys, and new magnetic materials. In order to understand the physical properties of any material, it is very important to know its electronic structure. For crystalline solids, modern band theoretical methods are usually very reliable in predicting electronic structures. However, for disordered alloys which do not possess full lattice periodicity, the usual band structure calculation methods cannot be employed since the Bloch theorem is inapplicable. Hence, various schemes, such as the rigid band model, the average *t*-matrix approximation, and coherent-potential approximation (CPA) have been devised to calculate the electronic structures of substitutional disordered alloys [1]. The CPA method is now most widely used and is known to predict electronic structures of various alloys fairly well. However, its validity is still often questioned, one notable example being the Cu-Pd alloy systems [2]. Hence, it is worthwhile to determine the electronic structures of disordered alloys

by experiments and to compare them with the results of theoretical calculations.

For the Cu-Pt alloy system, the *occupied* part of the electronic density of states (DOS) has been determined previously by photoelectron spectroscopy using synchrotron radiation [3]. The comparison with the results of the CPA calculation shows a fairly good agreement between theory and experiment, both for the Cu and the Pt partial densities of states. In this paper, we will complement this previous work by determining the *unoccupied* part of the electronic structures of the Cu-Pt alloys by bremsstrahlung isochromat spectroscopy (BIS). In particular, we observed the change of the Pt 5*d* state DOS as the Pt composition was changed. The result will test the consistency of the *occupied* part of the partial spectral weights obtained in the previous photoemission work. We will also measure various core-levels by X-ray photoelectron spectroscopy (XPS) to determine the amount of the charge transfer in the Cu-Pt alloy system. This will test the hypothesis of the negligible interatomic charge-transfer assumed in the published CPA calculation on the Cu-Pt alloys [4]. In that calculation, a computational difficulty prevented the construction of a self-consistent site potentials for the alloys, and hence the authors used the same potentials as for the pure metals, hoping that the charge transfer between the Cu and the Pt atoms was negligible.

II. EXPERIMENTAL

Polycrystalline $\text{Cu}_{1-x}\text{Pt}_x$ ($x=0, 0.10, 0.25, 0.50, 0.75,$

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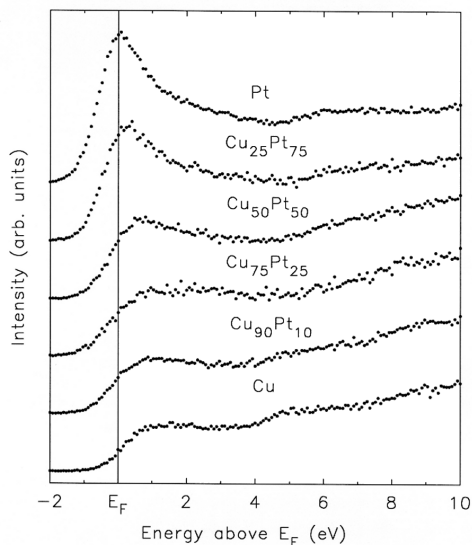


Fig. 1. BIS spectra of Cu_xPt_{1-x} alloys ($x=1.0, 0.90, 0.75, 0.50, 0.25,$ and 0.0).

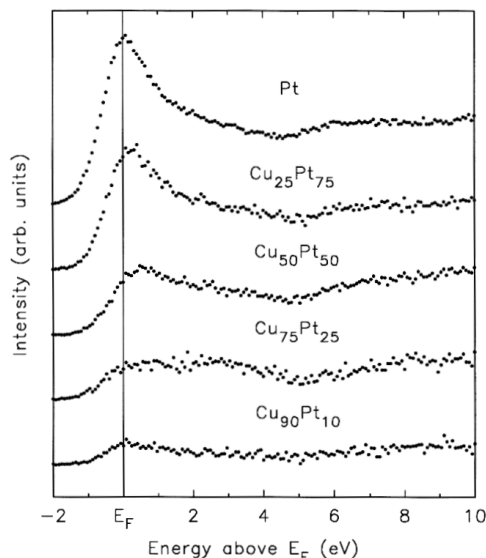


Fig. 3. Pt partial BIS spectra of Cu_xPt_{1-x} alloys after the subtraction procedure shown in Fig. 2.

and 1.0) alloy samples were made by melting high-purity Cu and Pt metals of appropriate amounts in an arc furnace under an argon atmosphere. In order to check the homogeneity of the samples, X-ray diffraction measurements were performed, which showed no additional phase [5]. In order to clean the sample surface for the XPS and the BIS measurements, scraping was done with a diamond file *in situ* at a base pressure better than 5×10^{-10} Torr. When the oxygen 1s or carbon 1s peak was found

to be non-negligible in the XPS spectrum, the sample surface was scraped again. XPS and BIS experiments were performed in an ultrahigh vacuum photoelectron spectrometer equipped with a 150-mm-radius hemispherical electron energy analyzer and Al K_{α} X-ray ($h\nu = 1486.6$ eV) monochromator. The total resolutions of the BIS

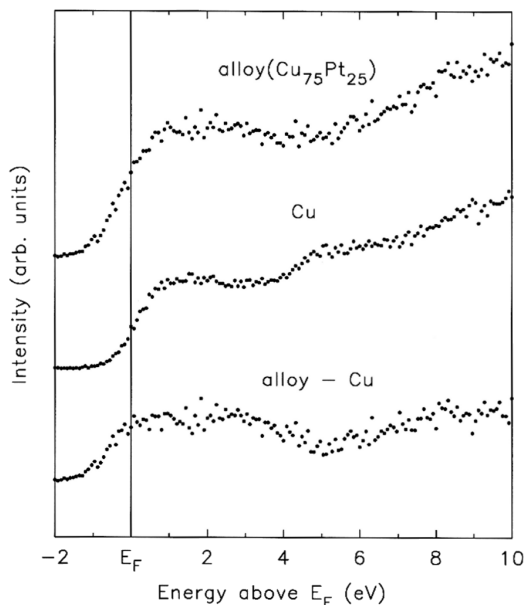


Fig. 2. Subtraction procedure to obtain the Pt partial BIS spectrum.

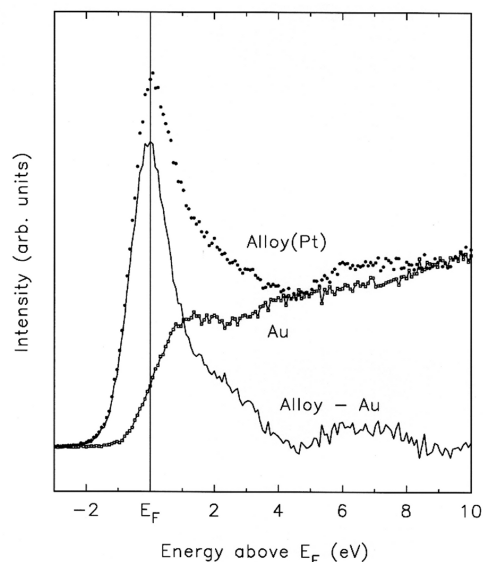


Fig. 4. Procedure to obtain the unoccupied Pt 5d band from the Pt and the Au pure metal BIS spectra. Dots and squares are Pt and Au metal BIS data, respectively, and the line represents the Pt 5d unoccupied density of states obtained by the subtraction of these two spectra.

Table 1. The values (in units of eV) of the measured core-level binding-energy shift $\Delta E(i)$, the work-function change $\Delta\Phi$, the final-state relaxation energy shift ΔE_r , and the change of the one-electron Hartree-Fock energy of the core-level i $\Delta\epsilon(i)$ for the Cu $2p_{3/2}$ (a) and Pt $4f_{7/2}$ (b) core-levels in Cu-Pt alloys at several compositions. The amount of the total inter-atomic charge transfer into the Cu (Pt) atom is δn^{Cu} (δn^{Pt}). The amount of the charge transfer into the $5d$ states of the Pt atom Δn_d (BIS) is obtained from the BIS experiment, as explained in Sec. III-1, and Δn_d for Cu is obtained from the calculation mentioned in Sec. III-2. (e is the magnitude of the fundamental charge.)

(a) Cu $2p_{3/2}$ level.						
Cu (at.%)	$\Delta E(i)$ (eV)	$\Delta\Phi$ (eV)	ΔE_r (eV)	$-\Delta\epsilon(i)$ (eV)	δn^{Cu} (e)	Δn_d (e)
100	0.00	0.00	0.00	0.00	0.00	0.00
90	-0.54	0.10	0.04	-0.38	0.02	-0.03
75	-0.66	0.25	0.11	-0.30	0.04	-0.02
50	-0.78	0.50	0.18	-0.10	0.01	-0.01
25	-1.44	0.75	0.28	-0.41	0.03	-0.03
(b) Pt $4f_{7/2}$ level.						
Pt (at.%)	$\Delta E(i)$ (eV)	$\Delta\Phi$ (eV)	ΔE_r (eV)	$-\Delta\epsilon(i)$ (eV)	δn^{Pt} (e)	Δn_d (BIS)(e)
100	0.0	0.00	0.00	0.00	0.00	0.00
75	0.0	-0.25	-0.25	-0.50	-0.01	0.083
50	0.0	-0.50	-0.53	-1.03	-0.01	0.18
25	0.0	-0.75	-0.89	-1.64	-0.11	0.20
10	0.0	-0.90	-1.28	-2.18	-0.16	0.25

and the XPS experiments were both about 1 eV (full width at half maximum).

III. EXPERIMENTAL DATA AND DISCUSSION

1. Unoccupied Electronic States Probed with BIS

BIS spectra of $\text{Cu}_{1-x}\text{Pt}_x$ ($x=0, 0.10, 0.25, 0.50, 0.75,$ and 1.0) alloys are shown in Fig. 1. We can clearly notice the reduction of the unoccupied DOS near E_F upon alloying with Cu, which is consistent with the behavior of occupied bands observed in the recent synchrotron radiation soft X-ray photoelectron spectroscopy [3] and the conventional XPS work [6]. These BIS spectra are normalized to have the same height at 6 eV above E_F because Cu or Pt d states are not expected to exist at that high energy and, therefore, the BIS intensity is mostly due to the Cu $4s$ and the Pt $6s$ levels. It turns out that the photoionization cross section of the Cu $4s$ state is similar to that of Pt $6s$ [7], so that the BIS intensity due to the Cu $4s$ and the Pt $6s$ states should remain almost the same, regardless of the alloy composition. The small bumps observed around 5 - 6 eV above E_F in the clean Cu and Pt spectra, which change slightly with the composition in the alloy samples, are due to the image state [8]. Since the image state does not reflect the densities of states, we will not concern ourselves with these structures here.

We are interested in the change of the unoccupied $5d$ state of Pt upon alloying with Cu. Hence, we need to

obtain the unoccupied Pt partial density of states from the BIS spectra. For this purpose, we use a simple subtraction procedure by assuming that the partial DOS of Cu does not change upon alloying. This assumption is certainly good for Cu-rich alloys, although it may become somewhat questionable for Pt-rich alloys. However, since the cross section of the Pt $5d$ state is more than 50 times larger than that of the Cu $4s$ state [7], a slight inaccuracy in the Cu $4s$ DOS will not have serious consequences. Hence, to obtain the Pt partial BIS spectra of the $\text{Cu}_x\text{Pt}_{1-x}$ alloy, we subtract the x fraction of the pure Cu BIS spectra from the alloy BIS spectra. The subtraction procedure of BIS spectra is the same as that in Ref. 14. Figure 2 illustrates this subtraction procedure for the $\text{Cu}_{0.75}\text{Pt}_{0.25}$ alloys.

Figure 3 shows the Pt partial BIS spectra of $\text{Cu}_x\text{Pt}_{1-x}$ alloys obtained by the method mentioned above. We can see that the Pt unoccupied band consists of a sharp peak near the Fermi level and a broad band extending to about 6 eV above the Fermi level. Considered as having a Pt $5d$ band character (the cross section of the Pt $6s$ state is much smaller [7] than that of the Pt $5d$ state), the sharp peak near the Fermi level can be assigned to the pure Pt “ $5d$ band”, and the broad band from the Fermi level to about 6 eV above the E_F can be assigned as the contribution from the Pt $5d$ state to the Pt $5d - 6sp$ hybridized band. We can see from Fig. 3 that the unoccupied Pt $5d$ band is reduced very clearly as the Pt content is decreased by alloying.

In order to determine quantitatively how much the number of unoccupied Pt $5d$ electron states ($5d$ holes) is reduced by alloying, we obtain the weight of the Pt

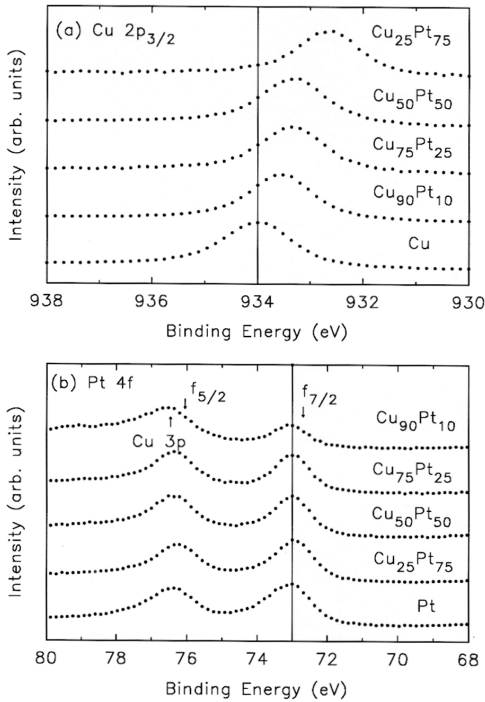


Fig. 5. (a) Cu $2p_{3/2}$ core-level binding-energy shift and (b) Pt $4f$ core-level binding-energy shift of $\text{Cu}_{1-x}\text{Pt}_x$ alloys measured by X-ray photoelectron spectroscopy.

$5d$ unoccupied states by subtracting the pure Au BIS spectrum from the alloy Pt partial BIS spectra of Fig. 3. This assumes that the $6s$ bands for Au and Pt are similar since Au is next to Pt in the periodic table and the Au $5d$ band is full. The procedure is shown in Fig. 4 for pure Pt metal, where the two spectra are aligned at 6 eV above the Fermi level. A similar subtraction procedure is carried out for the other alloys. From the area of the difference curve, we obtain the weight of the unoccupied Pt $5d$ levels, which in turn is converted to the number of Pt $5d$ holes n_d in the alloys by assuming that the number of Pt $5d$ holes in pure Pt metal is 0.30 electrons [9]. The change of the Pt $5d$ electron number for each alloy composition from that of the pure Pt metal as deduced from this analysis is written in the seventh column of Table 1(b) as $\Delta n_d(\text{BIS})$. It shows that the Pt $5d$ band is almost completely filled in the Pt-diluted limit (e.g. $\text{Cu}_{90}\text{Pt}_{10}$).

2. Core-Level Spectra with XPS

XPS core-level spectra of the Cu $2p_{3/2}$ and the Pt $4f_{7/2}$ levels for $\text{Cu}_x\text{Pt}_{1-x}$ alloys ($x = 0.00, 0.25, 0.50, 0.75, 0.90$, and 1.0) are shown in Fig. 5. In the case of the Pt $4f$ spectra in Fig. 5(b), the Cu $3p$ peak overlaps with the Pt $4f_{5/2}$ peak near 76 eV. This is the reason for

the apparently anomalous intensity ratio between the Pt $4f_{5/2}$ and $4f_{7/2}$ peaks for some Cu-rich $\text{Cu}_x\text{Pt}_{1-x}$ alloys. We have, therefore, analyzed the Pt $4f_{7/2}$ peak to observe the binding energy shift of the Pt core level. We can see from this figure that the Cu $2p_{3/2}$ peak is moved to lower binding energy by alloying with Pt, while the Pt $4f_{7/2}$ peak is hardly moved by alloying with Cu. These experimental findings are consistent with the previous XPS measurement on this alloy system [6]. However, quantitatively, the amount of the binding energy shift of the Cu $2p$ level as a function of the Pt concentration is a little larger in our measurement compared with that found in Ref. 6. This difference is probably due to the different surface cleaning methods in the two studies. In our present measurement, the sample surface was scraped *in situ* in order to obtain clean sample surfaces which had the same stoichiometry as the bulk, whereas the authors of Ref. 6 used the sputter-anneal method. It has been reported previously, based on Auger electron and ion-scattering spectroscopy works [10,11], that the annealed surfaces of Cu-Pt alloys become Cu-rich.

We obtained the amount of the binding energy shift $\Delta E(i)$ of the Cu $2p_{3/2}$ and the Pt $4f_{7/2}$ core-levels relative to the respective levels of the pure metal by a curve-fitting procedure using the Doniach-Sunjić lineshape, and the results are shown in Table 1. We can see that the Pt $4f$ level does not shift with alloy composition, whereas the Cu $2p$ level shifts to the low binding-energy side by as much as 1.44 eV upon alloying with Pt. This, however, does not necessarily mean that the charge flows from Pt to Cu. To interpret these data, we should understand several factors influencing the core-level binding energy measured by XPS [12,13].

First, it is important to realize that the experimental binding energy is measured relative to the Fermi level, whereas the Hartree Fock one-electron energy is referenced to the vacuum level. Second, the final-state relaxation energy after the core electron is ejected contributes significantly to the measured binding energy. Hence, the experimental binding energy shift $\Delta E(i)$ of the core level i between the pure metal and the alloy is related to the change of the Hartree-Fock one-electron energy $\Delta \epsilon(i)$ by the following equation [12–14]:

$$-\Delta \epsilon(i) = \Delta E(i) + \Delta E_F + \Delta E_r \quad (1)$$

where ΔE_F is the change of the Fermi level, and ΔE_r is the change of the relaxation energy in the presence of the core hole between the pure metal and the alloy. Usually, the Fermi-level change ΔE_F is replaced by the work-function change $\Delta \Phi$, which can be calculated assuming a linear dependence on the composition x . The work functions (averaged over the crystal planes) of the Cu and the Pt metals are known to be 4.65 eV and 5.65 eV, respectively [15], and the value of $\Delta \Phi$, thus, calculated as a function of the composition is shown in the 3rd column of Table 1. The final-state relaxation-energy term ΔE_r is usually difficult to estimate, and here we quote the results of a recent theoretical calculation [16] which

are listed in the fourth column of the same table. We see that in the case of the Pt $4f$ core-level, ΔE_r is much larger than the experimental binding energy shift $\Delta E(i)$. This implies that the final-state shift is as much important as the initial-state shift. We list the initial-state binding-energy shift $\Delta\epsilon(i)$ obtained using these values and Eq. (1) in the fifth column of Table 1.

To find the charge redistribution as a result of alloying, we use the following relation between the change of the Hartree-Fock one-electron energy of the core level i $\Delta\epsilon(i)$ and the change of the number of electrons in the ground state [12–14]:

$$\Delta\epsilon(i) = \Delta n_d F^0(i, d) + \Delta n_s F^0(i, s) - \delta n F_{latt}^0 \quad (2)$$

where $F^0(i, d)$ and $F^0(i, s)$ represent the Coulomb interaction between the core-electron i and the valence d electrons and that between the core-electron i and the valence s electrons, respectively. (Here, we do not distinguish the valence p electrons from the valence s electrons.) F_{latt}^0 is the Madelung term, and Δn_s and Δn_d represent the change of the number of s electrons and d electrons, respectively. Notice that we consider two kinds of charge redistributions that can occur as a result of alloying. One is the inter-atomic charge transfer between the Cu and the Pt atoms (denoted by δn here), and the other is the intra-atomic charge redistribution denoted by Δn_s or Δn_d .

The Coulomb interaction energies $F^0(i, d)$ and $F^0(i, s)$ and the Madelung energy F_{latt}^0 have been calculated already in Refs. 13, 17 and 14, respectively, so we will use those values. The change of the initial-state core-level Hartree-Fock energy $\Delta\epsilon(i)$ is calculated using Eq. (1) and is listed in the fifth column of Table 1. Furthermore, we have already obtained the change of the $5d$ electron number Δn_d in the Pt $5d$ band of the alloys from the analysis of the BIS spectra, and the results are listed in the last column of Table 1(b). With these values of the $F^0(i, d)$, the $F^0(i, s)$, and the F_{latt}^0 for the Pt atom and with the change of the number of unoccupied d electrons of the Pt atoms Δn_d , we can now calculate Δn_s of the Pt atom from Eq. (2). Then the amount of the (inter-atomic) total charge transfer $\delta n^{Pt} = \Delta n_d + \Delta n_s$ from the Pt atoms to the Cu atoms can be obtained, the results of which are summarized in the sixth column of Table 1(b).

We can also find the amount of the charge redistribution in the Cu atoms as follows: First, we can use the charge neutrality condition, which may be expressed by the following equation

$$(1-x)\delta n^{Cu} + x\delta n^{Pt} = 0, \quad (3)$$

to find the inter-atomic charge transfer from the Cu atoms to the Pt atoms δn^{Cu} . The results are listed in the sixth column of Table 1(a). These values can then be used to calculate the intra-atomic charge transfer Δn_d of the Cu atoms by using Eq. (2) and Eq. (3) applied to the Cu atom, the results of which are shown in the seventh column of Table 1(a).

We note several facts from Table 1. First, the amount of the inter-atomic charge transfer in the Cu-Pt alloy system is generally small, which is consistent with the assumption made in the earlier CPA calculation [4]. Second, the inter-atomic charge transfer is found to occur from the Pt atom to the Cu atom. Since the electronegativity [18] of Cu is 1.8, which is smaller than the value of 2.1 for Pt, this direction of the charge flow cannot be simply explained by the electronegativity difference. Third, in both the Pt and the Cu atoms, the sign of the inter-atomic charge transfer δn is opposite to that of the intra-atomic charge transfer of d electrons Δn_d . This means that the change of the number of d electrons as a result of alloying is more than compensated for by the s -electron redistribution. We believe this is the key point in understanding the change of the electronic structures due to alloying and the resulting charge redistribution in the Cu-Pt, and similar, alloy systems. Fourth, Table 1(a) shows that the Cu atom loses a few $3d$ electrons upon alloying with Pt. This is consistent with the Cu $3d$ partial spectral weights obtained in a recent synchrotron radiation photoemission study [3], where the Cu $3d$ band is shown to become broader and extend toward the Fermi level as the Pt concentration is increased due to the hybridization between Cu $3d$ and Pt $5d$ bands.

IV. CONCLUSIONS

In this paper, we have studied the unoccupied partial Pt $5d$ density of states in Cu-Pt alloys by bremsstrahlung isochromat spectroscopy and the charge redistribution effect in those alloys using the core-level shifts in the X-ray photoelectron spectroscopy. They all show the gradual filling of the Pt $5d$ band upon alloying with Cu and the Cu atom losing some $3d$ electrons in the Cu-diluted alloys. These are all consistent with the results of a recent synchrotron radiation photoemission spectroscopy study on the occupied electronic states of this alloy system.

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