Electronic Structures of Amorphous Co-P and Ni-P Alloys by γ-ray Compton Scattering

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Toshihisa Honda, Fumitake Itoh, Toshiharu Fukunaga
and Kenji Suzuki

The Research Institute for Iron, Steel and Other metals
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Synopsis

γ-ray Compton scattering has been applied to study the electronic state of electro-deposited and melt-quenched amorphous $Ni_{81}P_{19}$ alloys, and electro-deposited amorphous $Co_{82}P_{18}$ alloy. Based on experimental Compton profiles, it is conclused that the charge transfer occurs from phosphorus atom to 3d band holes of transition metals, but 3d states may not be completely filled with electrons even in amorphous $Ni_{81}P_{19}$ alloy.

I. Introduction

Many investigations of atomic structure and magnetic properties have been focused on amorphous transition metal-metalloid alloys because of their superior abilities as device engineering materials in near future. Based on magnetic measurements the elctronic structure of amorphous transition metal-metalloid alloys has been explained in terms of charge transfer from metalloid atom to 3d band holes of transition metals.[1)]

As amorphous solids are not in the thermodynamic equlibrium state, the atomic structure and physical properties of amorphous solids depend on their histories including preparation procedures. For example, electro-deposited(ED) amorphous Ni-P alloys are brittle, whereas

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melt-quenched(MQ) amorphous Ni-P alloys have a good ductility and toughness.

In this study the measurement of Compton profiles is applied to investigate the electronic structure of amorphous $Ni_{81}P_{19}$ and $Co_{82}P_{18}$ alloys prepared through different processes.

During last ten years Compton scattering studies have been extensively developed in both the theoretical and experimental fields and established as a powerful technique to obtain directly the information on electronic structures of various kinds of meterials.[2)]

Within the framework of impulse approximation[3)], Compton profile $J(q)$ is directly related to the electronic momentum density $n(\vec{p})$ in a specimen; i.e.

$$J(q) = \int_{-\infty}^{\infty}\int n(\vec{p})\, dp_x dp_y \quad (q=p_z) \tag{1}$$

and

$$n(\vec{p}) = | \chi(\vec{p})^* \chi(\vec{p}) | \tag{2}$$

where q means the projection of ground state electron momentum $\vec{p}=(p_x,p_y,p_z)$ on the scattering vector and $\chi(\vec{p})$ is the momentum wavefunction defined as a Fourier transform of real space wavefunction $\Psi(\vec{r})$ as follows

$$\chi(\vec{p}) = (2\pi)^{-3/2} \int \Psi(\vec{r}) \cdot \exp(-i\vec{p}\vec{r})\, d\vec{r} \tag{3}$$

Therefore we can directly measure the nature of chemical bonding, charge transfer and so on even in disordered materials using Compton scattering technique.

II. Experimental

Amorphous $Ni_{81}P_{19}$ and $Co_{82}P_{18}$ alloys in a form of thin plate of about 75μm in thickness were prepared by electro-deposition. Details of electro-deposition procedure are almost same to the method used originally by Brenner et al.[4)] Phosphorus contents in the both alloys were precisely determined as Ni-18.9 at%P and Co-18.25 at%P respective-

ly by the conventional chemical analysis.

After finishing the measurement of the Compton scattering for the ED amorphous $Ni_{81}P_{19}$ alloy, this alloy was melt in argon atmosphere and then melt-quenched using a single roll method. The thickness of MQ amorphous $Ni_{81}P_{19}$ alloy is in the range of 10 to 15 μm. After completing all the measurements of the Compton scattering for amorphous alloys, the alloys were crystallized by annealing them at 600°C for 5 hours and then Compton profiles for their crystallized states were measured.

Measurements of all Compton profiles were carried out using 59.54 keV γ-rays emitted from ^{241}Am radioisotope and a Ge solid state detector. The experimental apparatus used in this study is almost identical to that described in a previous paper[5] except for a sample holder. In the case of the measurement of the Compton profile for red phosphorus powder a sample vessel of 1 mm in thickness with mylar windows of 5 μm in thickness was used.

The background correction for mylar windows were made. The multiple scattering correction described elsewhere[5,6] was neglected in this study, because the thickness of the sample was thin enough to avoid the distortion of observed Compton profiles. The deconvolution of an experimental resolution function was applied to raw profiles by generalized least squares method of Fourier analysis[5] using k=3 and λ=300 in eq. (3-6) of Ref.7. Details of the performance of the Compton scattering spectrometer and the data processing procedures have been fully described in the previous paper.[5]

The final Compton profile for each sample was normalized to the half value of normelization value N' over the range of q(a.u.) from 0 to 6.0 a.u. for $Ni_{81}P_{19}$ alloys and 4.5 a.u. for $Co_{82}P_{18}$ alloys. The normalization value N' is equal to the area under the theoretical profile calculated from Clementi's free atom wavefunctions.[7] The experimental conditions in this study are summalized in Tables I and II for $Ni_{81}P_{19}$ and $Co_{82}P_{18}$ alloys, respectively.

III. Results

Figure 1 shows experimental Compton profiles of pure nickel (closed circles) and phosphorus (open circles) together with two theoretical profiles for nickel metal. Solid curves in Figure 1 indicate theoretical profiles for core electrons of nickel (labeled 3d(8)) and phosphorus (labeled KL), which are constituted with the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ for nickel and $1s^2 2s^2 2p^6$ for

Table I. Experimental conditions of the Compton profile measurements and normalization values in the maximum range 6 a.u. for nickel metal, phosphorus and Ni-P alloys. The letters "A" and "C" mean the amorphous and crystallized state, respectively.

Sample	Ni-P	Ni-P	Ni-P	Ni-P	Ni	P
State	A	C	A	C	-	-
Preparatin	ED	ED	MQ	MQ	-	-
Measurement time (day)	13.7	13.4	15.5	14.7	12.6	7.5
Peak counts	57,200	53,900	51,000	40,000	54,500	60,000
Thickness (mm)	0.15	0.15	0.15	0.15	0.15	1.0
Density(g/cc)	8.10	8.20	8.01	8.20	8.85	2.20
Normalization value N'	21.871	21.871	21.871	21.871	23.764	13.749

Table II. Experimental conditions of the Compton profile measurement and normalization values for cobalt metal, phosphorus and Co-P alloys.

Sample	Co-P	Co-P	Co	P
State	A	C	-	-
Measurement time (day)	24.1	25.7	35.8	19.6
Peak counts	9,700	12,200	11,900	29,300
Density (g/cc)	8.31	8.31	8.90	2.20
Normalization value N'	19.871	19.871	21.403	13.00

phosphorus by Clementi's free atom wavefunctions.[7] In higher momentum region of q>2.5 a.u., the calculated core electron profiles are in fair agreement with the experimental ones.

The dotted curves in Figure 1 indicates the free electron(FE) model with two conduction electrons per nickel atom. The broken curve

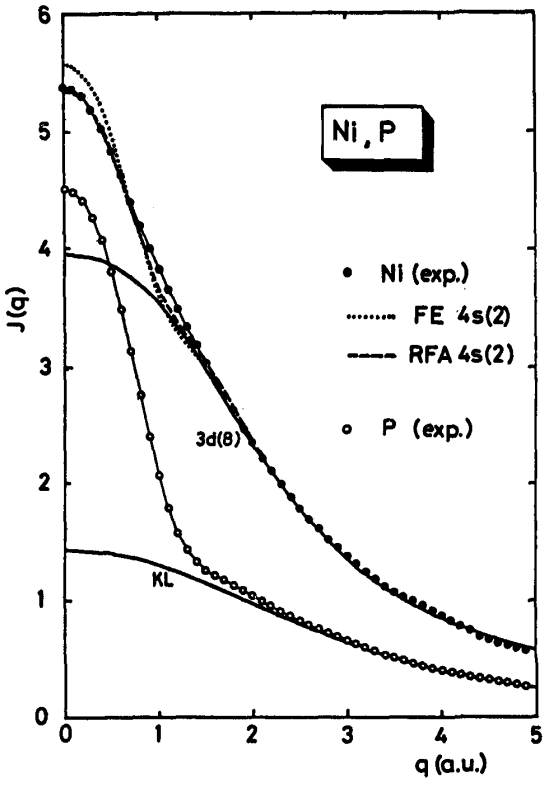

Fig.1. Experimental and theoretical Compton profiles for nickel metal and phosphorus powder. Closed circles and open circles represent the experimental profile for nickel metal and phosphorus ,respectively. The broken and dotted curces show the theoretical profile for nickel metal based on the renormalized free atom (RFA) model and the free electron (FE) model, respectively. Solid curves indicate the theoretical profiles for core electrons.

shows the another theoretical profile calculated by following the renormelized free atom (RFA) model by Berggren[8], in which 4s free atom wavefunctions[7] are truncated at the radius of the Wigner-Seitz sphere and then normalized within the sphere therby preserving charge neutrality. Both theoretical profiles are convoluted with the residual instrument function (RIF)[5,9] in this study.

The RFA model is in good agreement with the experimental Compton profile for nickel metal compared to the FE model. However, an appreciable discrepancy between the experiment and both theoretical profiles

can be found over an intermediate momentum region around q=1.0 a.u.

Figure 2 shows the experimental Compton profile for ED amorphous $Ni_{81}P_{19}$ alloy denoted by open circles. The solid curve denotes the weighted sum of experimental Compton profiles for pure nickel metal and phosphorus; i.e. $0.811\ J_{Ni}^{exp.} + 0.189\ J_{P}^{exp.}$. The dotted and dashed curves in Figure 2 indicate the theoretical profiles for $Ni_{81}P_{19}$ alloy which will be described in next section.

As can be seen in Figure 2 , there is some difference between the experimental Compton profile for ED amorphous $Ni_{81}P_{19}$ alloy and the weighted sum of experimental profiles for constituent elements in lower momentum region of q<1.0 a.u. This discrepancy arises due to the

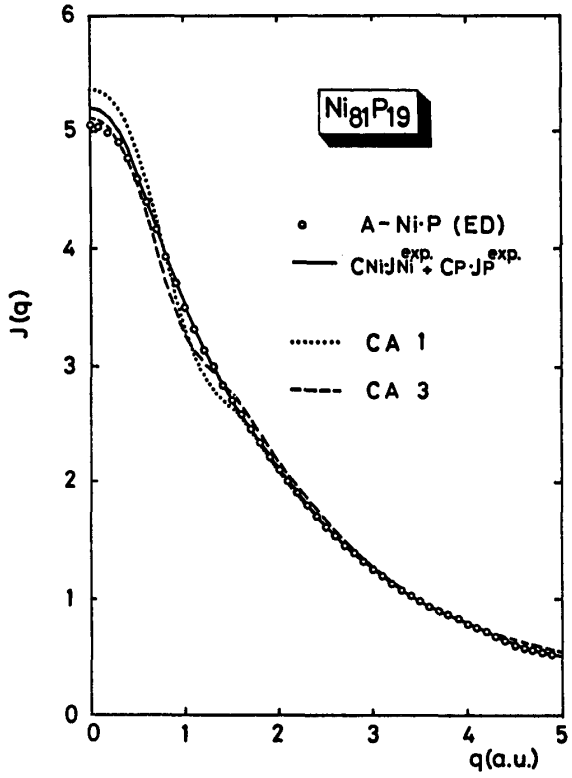

Fig.2. Experimental Compton profile for ED amorphous $Ni_{81}P_{19}$ alloy (open circles). The solid curve represents the weighted sum of experimental profiles for constituent elements. The dotted and broken curves indicate model CA1 and CA3, respectively, of which electronic configurations are given in the text.

change in the electronic structure upon alloying. In order to show more clearly the alloying effect, differential curves between experimental profiles for four kinds of $Ni_{81}P_{19}$ alloys and the weighted sum of experimental profiles for constituent elements; i.e. $J_{Ni-P}^{exp.} - (0.811\ J_{Ni}^{exp.} + 0.189\ J_{P}^{exp.})$ are plotted in Figure 3. Letter A and C in Figure 3 denote the amorphous and crystallized states, respectively.

Figure 3 means that experimental Compton profiles for ED and MQ $Ni_{81}P_{19}$ alloys and their crystallized alloys are almost same each other within the experimental uncertainty in this study. Therefore there seems no difference in electronic structures between ED $Ni_{81}P_{19}$ alloy and MQ one.

All the differential curves in Figure 3 show negative values near zero momentum region but reverse their signs over intermediate momentum region and reach maxima around q=1.0 a.u., beyond which the curves gradually approarch zero in higher momentum region of q>2.5 a.u.

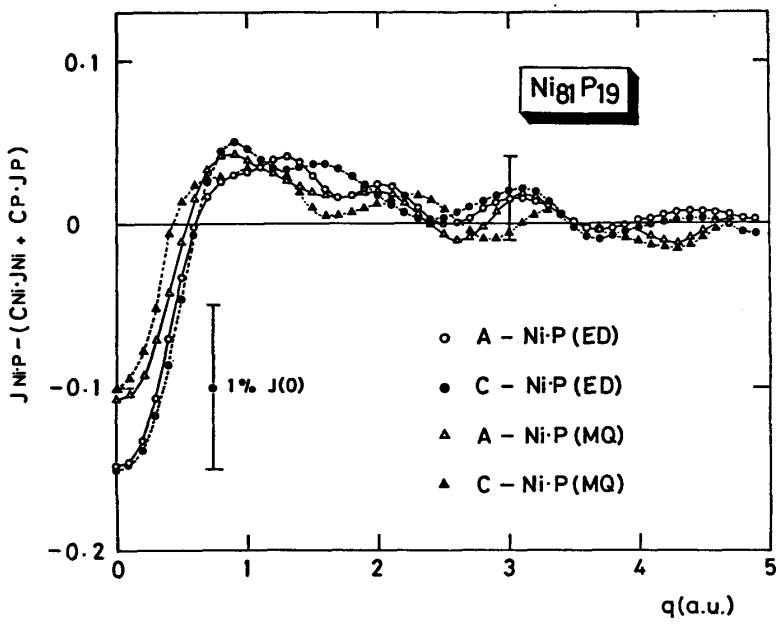

Fig.3. Differential curves between experimental profiles for four kinds of $Ni_{81}P_{19}$ alloys and the weighted sum of experimental profiles for constituent elements.

Experimental Compton profile for cobalt metal(closed circles) and two theoretical profiles are shown in Figure 4. The broken curve in Figure 4 represents the theoretical profile for core electrons($1s^2 2s^2$

$2p^6 3s^2 3d^7$) of cobalt metal calculated using free atom wavefunctions by Clementi.[7] The experimental profile is in good agreement with the core electron profile over higher momentum region of q>1.5 a.u.

The dotted and dashed curves indicate the FE model with two conduction electrons per atom and the RFA model, respectively. In the RFA scheme for cobalt metal, the momentum density was represented for a HCP crystal structure.[11] In contrast to nickel metal, the agreement between the RFA model and experimental result for cobelt metal is not so good.

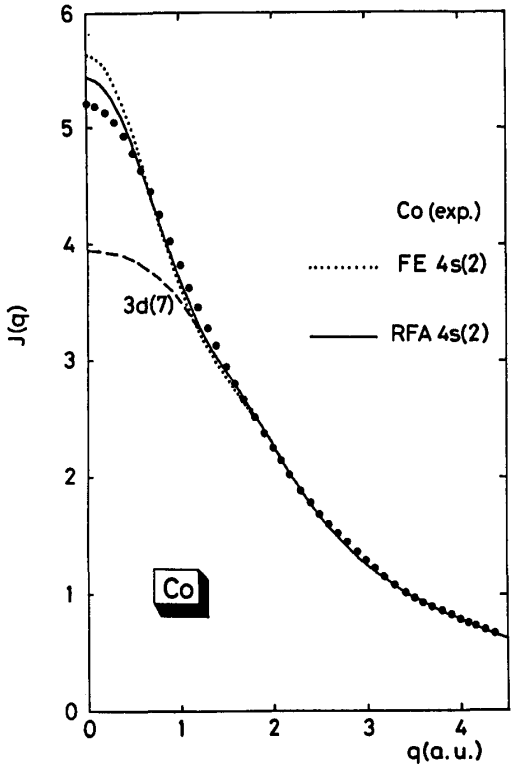

Fig.4. Experimental and theoretical Compton profiles for cobalt metal. Closed circles represent the experimental profile. The dotted and solid curves denote the FE model and the RFA model, respectively. The broken curve shows the theoretical profile for core electrons.

Figure 5 shows differential curves between the experimental Compton profile for $Co_{82}P_{18}$ alloy and the weighted sum of experimental

profiles for ED amorphous $Co_{82}P_{18}$ alloy and its crystallized state, respectively. The overall feature of the differential curves in Figure 5 is similar to that of $Ni_{81}P_{19}$ alloys as shown in Figure 3.

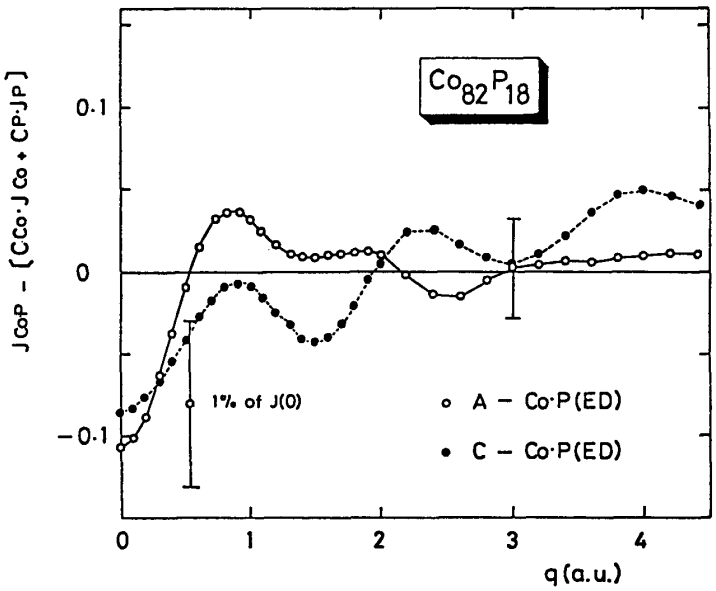

Fig.5. Differential curves between experimental profiles for ED amorphous and crystallized $Co_{82}P_{18}$ alloys and the weighted sum of experimental profiles for constituent elements. Letter "A" and "C" indicate the amorphous and crystallized states, respectively.

IV. Discussion

In order to understand the behavior of experimental differential curves shown in Figure 3, we make theoretical Compton profiles based on electronic structure models for $Ni_{81}P_{19}$ and $Co_{82}P_{18}$ alloys. Here, it is assumed for simplicity that the conduction electrons in the both alloys are free electrons and the core electrons are same to those of free atoms. Four different kinds of model profiles for $Ni_{81}P_{19}$ and $Co_{82}P_{18}$ alloys are discussed according to the nature of charge transfer between transition metal and phosphorus atom in the alloys. Electronic configurations for each model profiles are listed in Table III and IV.

Model CA2 and CA3 indicate that a part of valence electrons of phosphorus atom are transfered to 3d band holes of nickel or cobalt

atom. Model AN1 indicates the charge transfer of conduction electrons from transition metals to the outer shell of phosphorus atom upon alloying. Model CA1 means no change in the 3d band of transition metals.

Table III. Electronic configurations for model profiles for $Ni_{81}P_{19}$ alloy. The core electron profiles are calculated using the free atom wavefunctions by Clementi.[7] Conduction electrons are assumed to be free electrons.

Model	Electronic Configuration	
	Core	Conduction
CA1	Ni : KL + $3s^2 3p^6 3d^8$	
	P : KL + $3s^2$	2.19 FE
CA2	Ni : KL + $3s^2 3p^6 3d^{8.4}$	
	P : KL	2.24 FE
CA3	Ni : KL + $3s^2 3p^6 3d^9$	
	P : KL	1.76 FE
AN1	Ni : KL + $3s^2 3p^6 3d^8$	
	P : KL + $3s^2 3p^4$	1.43 FE

Table IV. Electronic configurations for model profiles for $Co_{82}P_{18}$ alloy. The core electron profiles are calculated using the free atom wavefunctions by Clementi.[7] Conduction electrons in the Co-P alloy are assumed to be free electrons.

Model	Electronic configuration	
	Core	Conduction
CA1	Co : KL + $3s^2 3p^6 3d^7$	
	P : KL	2.55 FE
CA2	Co : KL + $3s^2 3p^6 3d^{7.5}$	
	P : KL	2.14 FE
CA3	Co : KL + $3s^2 3p^6 3d^8$	
	P : KL	1.73 FE
AN1	Co : KL + $3s^2 3p^6 3d^7$	
	P : KL + $3s^2 3p^4$	1.45 FE

Theoretical Compton profiles of model CA1 and CA3 for $Ni_{81}P_{19}$ alloy are shown in Figure 2 by the dotted and broken curves, respectively. Both theoretical profiles have been convoluted with the RIF in this study.

Theoretical differential curves between the model profiles for amorphous $Ni_{81}P_{19}$ alloy and the weighted sum of the model profiles for nickel metal and the experimental profile for phosphorus are presented in Figure 6. Here, we have adopted the FE model as a model profile for nickel metal and the experimental profile as a model profile for phosphorus through lack of a good theoretical profile so far. Same theoretical curves for amorphous $Co_{82}P_{18}$ alloy are shown in Figure 7.

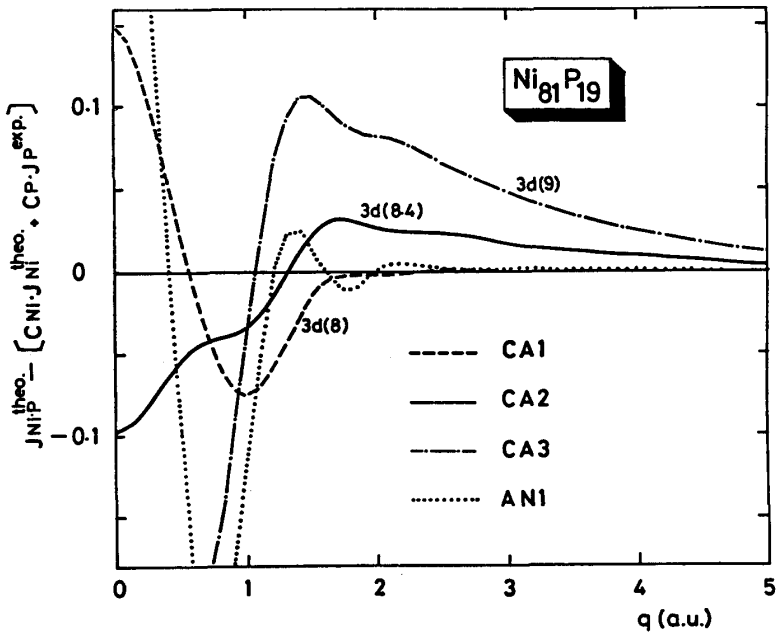

Fig.6. Theoretical differential curves between the model profiles for amorphous $Ni_{81}P_{19}$ alloy and the weighted sum of the model profile for nickel metal and the experimental profile for phosphorus.

From the comparison of differential curves between the experimental(Figures 3 and 4) and the theoretical (Figures 6 and 7), model CA2 is in best agreement with the experimental differential curves in the both alloys. Hence, it is suggested that a part of valence electrons of phosphorus atom are transfered to 3d band holes of transition metals and accordingly the number of 3d electrons in amorphous alloys is in-

creased rather than that in pure transition metal upon alloying. This conclusion by the present Compton scattering experiment is consistent with the electronic structure obtained from the magnetic measurements for amorphous transion metal-metalloid alloys.[1)]

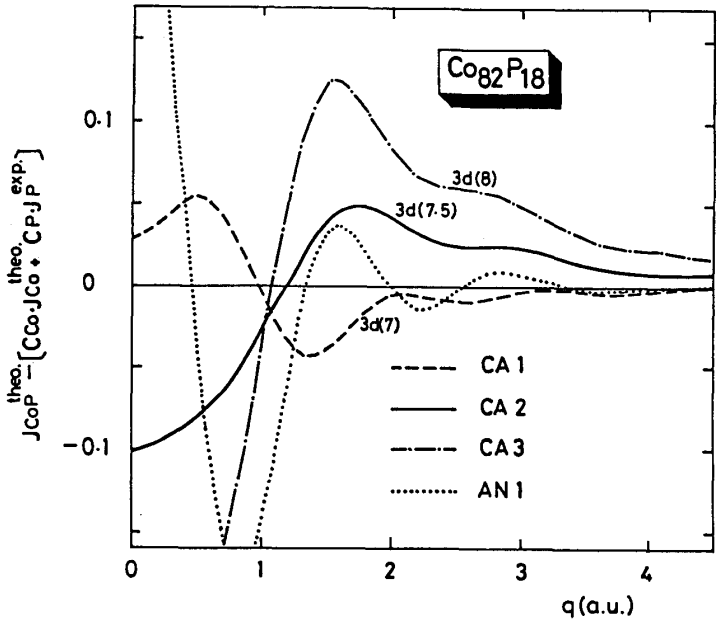

Fig.7. Theoretical differential curves between the model profiles for amorphous $Co_{82}P_{18}$ alloy and the weighted sum of the model profile for cobalt metal and the experimental profile for phosphorus.

The magnetic moment of amorphous $Ni_{81}P_{19}$ alloy is known to be almost zero.[1,12,13)] This may indicate that the 3d band of nickel metal must be completely filled with electrons according to the charge transfer model based on a simple rigid band model. On the other hand, the number of 3d electrons estimated from the present Compton scattering experiment is less than ten in amorphous $Ni_{81}P_{19}$ alloy. Therefore, it is possible to consider that the number of 3d electrons in up-spin and down-spin subbands is balanced in amorphous $Ni_{81}P_{19}$ alloy, while an unbalance happens in amorphous $Co_{82}P_{18}$ alloy.

As shown Figure 1, the 3d electron number in nickel metal estimated from its Compton profile is 8 electrons/atom which is less than the electron number accepted generally of 9.46 electrons/atom.[14)] Since the Compton profile in Figure 6 yields the 3d electron number

in nickel in amorphous $Ni_{81}P_{19}$ alloy of 8.4 electrons/atom, the 3d band of nickel may be full in amorphous $Ni_{81}P_{19}$ alloy because 0.5 3d electrons are added to the 3d band of nickel metal.

The free atom approximation used in this discussion is supposed to be too simple to describe the 3d electron wavefunctions in amorphous transition metal-metalloid alloys. Therefore the conclusive remark about the electron number in 3d band is quite limited.

Recently, XPS[15,16] and Compton scattering[17] have been measured about amorphous transition metal (iron and cobalt)-boron alloys, in which the formation of new chemical bonding states is found between 3d electrons in transition metal atom and p electrons in metalloid atom. On the other hand, XPS[10] of amorphous $Ni_{81}P_{19}$ alloy, which is the same sample used in this study, does not show any bonding states over lower energy side of 3d band. Therefore,the electronic structure of amorphous Ni-P and Co-P alloys can be essentially interpreted in terms of the charge transfer from phosphorus to 3d band holes of transition metals.

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