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II. 1. $L_{\gamma1}$ x-ray Intensity Change in Proton Excited Nb Metal, Alloys and Compounds

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Introduction

Our Tohoku University group reported x-ray intensity change by the chemical environment [1-4]. X-ray intensity ratios of many compounds are changed by their chemical environments in these reports. The change is discussed in terms of oxidation number, ionicity or occupation. In metals, however, the chemical effect could not be explained with these parameters. For example, the K_α/K_β intensity ratio of chromium metal whose formal oxidation number is zero is similar to the value of the chromium(III) compounds .

In a previous paper[5] we have reported the intensity change in niobium and molybdenum compounds. The $L_{\gamma1}/L_{\beta1}$ intensity ratios by proton or electron excitation were dependent on the electron density due to the formation of molecular orbital. This tendency was found almost the same in both excitation methods, but notable exception was in the case of metallic Nb or Mo.

In this work we measured niobium L x-ray spectra in some niobium compounds and Nb-Ni amorphous alloys to explain the difference of $L_{\gamma1}/L_{\beta1}$ x-ray intensity ratios between proton and electron excitation.

Experimental

L x-rays of niobium were measured for Nb-Ni amorphous alloy, metallic Nb, NbN and NbC. Used Nb-Ni amorphous alloys have three different compositions: $Nb_{0.5}Ni_{0.5}$, $Nb_{0.4}Ni_{0.6}$, and $Nb_{0.3}Ni_{0.7}$. These alloys prepared by Dr. Aoki, Tohoku Univ. were of ribbon form which was 1 mm width and 0.1 mm thickness. Metallic Nb was a foil with 10 μm thickness. Other chemicals were of powder form, and were pressed into a disc on an aluminum ring with 30 mm diameter for x-ray excitation and into the disc with 13 mm diameter and 0.5 mm thickness for proton excitation.

X-ray spectra were measured with three different spectrometers, a Johannson type curved crystal spectrometer, a position sensitive type spectrometer and a double crystal spectrometer. A Johannson type and a position sensitive type spectrometers are installed at

Cyclotron and Radioisotope Center, Tohoku University. An ADP (101), a TlAP and two Ge (111) crystals were used for the measurements. A double crystal spectrometer was used to measure $L_{\gamma 1}$ fine structure by X-ray excitation with a Cu x-ray tube (20 kV, 140 mA). 3 MeV proton excitation spectra were obtained by a Johannson type and a position sensitive type spectrometer. A Johannson type spectrometer was used in 11 keV electron bombardment.

Results

Figure 1 shows an example of the spectrum of niobium L x-ray measured with a position sensitive spectrometer. We can see that L_α , $L_{\beta 1}$, $L_{\gamma 1}$ and other peaks are separated to each other. The spectra which were measured with a Johannson type spectrometer were shown in the previous report$^{5)}$. The resolution of these spectrometer is about 10 eV at $L_{\beta 1}$. Measured spectra were analyzed with Voigt functions and $L_{\gamma 1}/L_{\beta 1}$, intensity ratios were calculated from the peak areas.

Figure 2 shows Nb $L_{\gamma 1}$ spectra of metallic Nb and Nb-Ni amorphous alloys measured with a double-crystal spectrometer by x-ray excitation. The $L_{\gamma 1}$ peaks in the spectra of metallic Nb and Nb-Ni amorphous alloy are considered to be broadened. These spectra were fitted with a half-Lorentzian function. An asymmetry parameter is calculated from the FWHM of low energy part divided by that of high energy part.

Table 1 shows the $L_{\gamma 1}/L_{\beta 1}$ intensity ratios which are corrected to the absorption, FWHM change and asymmetry parameters of $L_{\gamma 1}$. We can see the differences of $L_{\gamma 1}/L_{\beta 1}$ between proton excitation and other excitations in metallic Nb and Nb-Ni amorphous alloys. In proton excitation, $L_{\gamma 1}/L_{\beta 1}$ values of metallic Nb and Nb-Ni amorphous alloys are smaller than that obtained by other excitation methods.

Discussion

$L_{\gamma 1}/L_{\beta 1}$ ratios by electron or x-ray excitation are as large as that by proton excitation in the case of NbC and NbN. And the tendency of the ratios, NbC < NbN, is commonly observed in all the excitation methods. However in metallic Nb, $L_{\gamma 1}/L_{\beta 1}$ by proton excitation is about half as large as that by electron or x-ray excitation as shown in Table 1 and also in Table 2. Also in Nb-Ni amorphous alloys, the $L_{\gamma 1}/L_{\beta 1}$ ratio has the same tendency as metallic Nb, but the decrease of the ratio is only slight.

These differences of the $L_{\gamma 1}/L_{\beta 1}$ ratios are considered to be caused by the differences of valence electron densities due to the difference of excitation method. The decrease of the valence electron density in metallic Nb seems to be caused by multiple ionization. The multiple ionization cross section for inner shell and valence shell electrons in proton excitation is much larger than in electron or x-ray excitation in this experimental condition. And this cross section depends on the energy gap between the valence band and the conduction band. This energy gap is very small in metallic compounds, while it is generally large in ionic or covalent compounds. So the order of the multiple ionization cross section of a valence electron is metallic Nb > Nb-Ni amorphous alloy > NbC ~ NbN. This order shows the order of the decrease of $L_{\gamma1}/L_{\beta1}$ ratios.

Acknowledgment

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Table. 1. $L_{\gamma1}/L_{\beta1}$ of niobium for various Nb samples.

Target	$L_{\gamma1}/L_{\beta1}/10^{-2}$		asymmetry parameter
	3MeV p*	X-ray Tube	
metallic Nb	1.7±0.1	3.12±0.07	1.53±0.03
$Nb_{0.5}Ni_{0.5}$	2.3±0.3	2.35±0.10	1.13±0.14
$Nb_{0.4}Ni_{0.6}$	2.1±0.5	2.72±0.20	1.07±0.07
$Nb_{0.3}Ni_{0.7}$	2.5±0.5	2.82±0.21	1.11±0.04
NbC	—	2.41±0.12	-
NbN	—	3.88±0.15	-

* measured with a position sensitive type spectrometer

Table. 2. $L_{\gamma1}/L_{\beta1}$ ratios by proton and electron excitations measured with a Johannson tipe spectrometer[5].

sample	$L_{\gamma1}/L_{\beta1}/10^{-2}$	
	11keV e⁻	3MeV p
metallic Nb	3.20±0.19	1.56±0.11
NbC	2.51±0.13	2.67±0.03
NbN	2.83±0.22	3.04±0.11

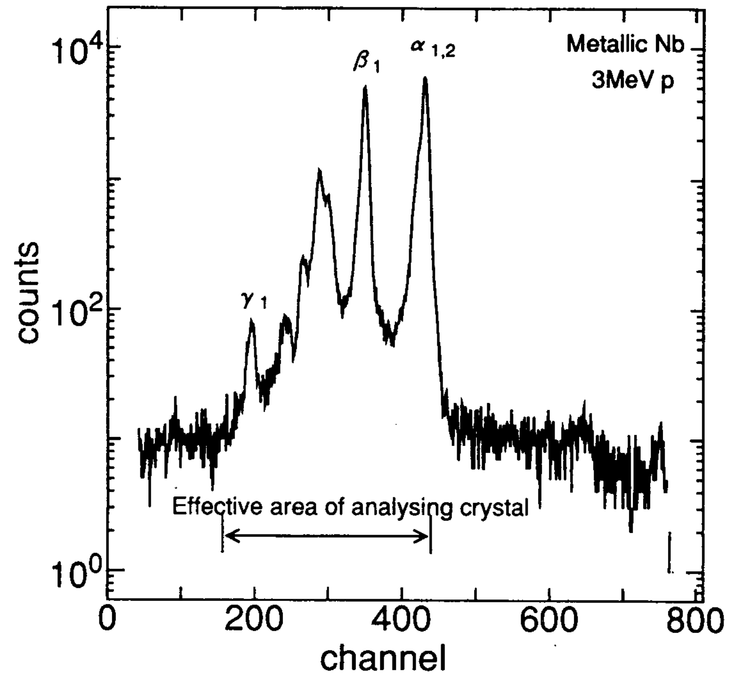

Fig. 1. L x-ray spectrum of metallic Nb measured with position sensitive spectrometer.

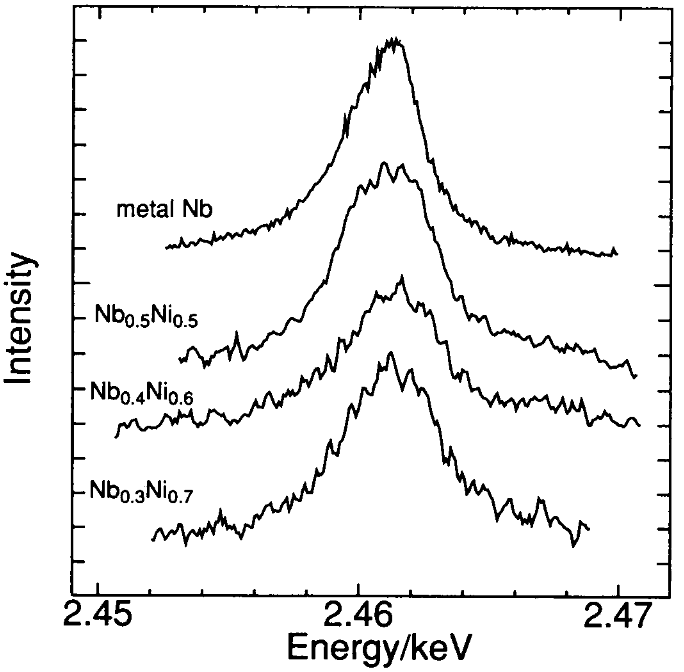

Fig. 2. High resolution $L_{\gamma 1}$ spectra of metallic Nb and Nb-Ni amorphous alloys.