Chemical Effects of L X-Ray Intensity Ratios in Niobium and Molybdenum Compounds by Elecron and Proton Bombardments

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1. Introduction

In the previous reports[1,2], chemical effect of the $L_{\gamma1}/L_{\beta1}$ intensity ratio has been established in the niobium and molybdenum compounds. Especially, in the case of NbC, NbN and NbO, of which crystal structure belongs to NaCl type, the $L_{\gamma1}/L_{\beta1}$ intensity ratio could be related to the 4d electron density. This was supported by the chemical environment, where emissions of L_{η} and $L_{\beta1}$ lines are associated with the inner shell transition.

In the present work, chemical effect of L X-ray spectrum will further be studied in the niobium and molybdenum compounds by 11 keV electron and 3 MeV proton bombardments. The $L_{\gamma1}/L_{\beta1}$ intensity ratio will be discussed on the basis of 4d electron density calculated by the GAMESS MO method.

2. Experimental

The purity of the chemicals was higher than 99.5 %. All the chemicals in powder were compressed to discs of 0.5 mm in the thickness and 13 mm in the diameter. The excitation of the target was carried out with 11 keV electrons using an electron gun and with 3 MeV protons using a cyclotron. The sample chamber was held lower than 10^{-5} Torr. The x-rays were measured with a Johansson-type crystal spectrometer with an ADP crystal (2d = 1.0646 nm). The radius of Rowland circle was 127 mm and the detector was Kr-gas enclosed type with a 0.0254 mm Be window. The wave length was scanned by monitoring the electron and proton beam currents. The time of measurement was set to be over 50000 counts at the $L_{\beta1}$ line. The control of spectrometer and the data transfer were carried out with a microcomputer PDP11/05.

3. Results and Discussion

As a typical example, the measured and profile-fitted Lx-ray spectrum of niobium in NbC is shown in Fig. 1. The profile fitting of measured spectrum was carried out with the Voigt function[3] expressed in Eq. (1).

$$C(X) = A \int_{-\infty}^{\infty} \frac{\exp(\alpha X'^2)}{(\Gamma_L/2)^2+(X-X'-X_0)^2} dX' \tag{1}$$

$$\alpha = -\frac{1}{2\Gamma_G^2} \tag{2}$$

where X is the x-ray energy, X_0 is the peak energy, A is the peak height, Γ_L is the FWHM of the curve and Γ_G represents the detector resolution. The profile fitting was carried out using an ACOS 2000 at the Computer Center, Tohoku University, with a non-linear least squares method. Satellite peaks following the Coster-Kronig transition appear 10 eV higher than those of $L_{\alpha 1,2}$ and $L_{\beta 1}$.[4] The $L_{\gamma 1}/L_{\beta 1}$ intensity ratio was obtained by dividing the peak area of $L_{\gamma 1}$ with $L_{\beta 1}$. In the electron beam bombardment, there was no effect of x-ray self-absorption, since the maximum inner range of 11 keV electron is 1.97×10^{-4} g/cm^2.[5] On the other hand, the effect of x-ray self-absorption should be considered in the proton beam bombardment. Thus, necessary corrections were done for the proton energy loss[6], x-ray production cross-section[8] and x-ray self-absorption.[9] L_η ($L_{II}M_I$) and $L_{\beta 1}$ ($L_{II}M_{IV}$) are due to the transition between inner shells. The $L_\eta/L_{\beta 1}$ intensity ratio is proved to be constant without respect to the niobium and molybdenum compounds. Therefore the inner shells are not affected by the chemical states of niobium and molybdenum atom. The $L_{\gamma 1}/L_{\beta 1}$ intensity ratio varies by the compounds. This feature suggests that the valence shell is affected by the chemical state of niobium atom.

The x-ray intensity, T, is given by the following equation.[10]

$$T = AN_iE_x^3D_{i,j}^2 \tag{3}$$

where N_i is the density of electrons in the initial orbital i and E_x is the x-ray transition energy and $D_{i,j}$ is the dipole matrix element in atomic units. The subscripts i and j indicate the initial orbital and final orbital, respectively, in x-ray emission. Energy shift of niobium or molybdenum Lx-ray does not influence to intensity change, because it is less than 1 eV. The dipole matrix element, $D_{i,j}$, is considered to be constant for all niobium or molybdenum compounds. $L_{\gamma 1}$ intensity change is considered to be effected by the 4d electron density change caused by making chemical bonding. The molecular orbitals of niobium compounds were calculated by the GAMESS MO calculation method. The MO calculation was done using a SX-2N at the Computer Center, Tohoku University. The basis set used was STO-2G for all species for relative comparison. The model of the MO calculation was a centered niobium or molybdenum with the nearest surrounding atoms. An example of Mulliken and Lowdin population analysis for NbC is listed in Table 1. The molecular orbital which participates in the emission of $L_{\gamma 1}$ x-rays was assigned to be $2t_{2g}$. Thus, the occupation of the 4d orbital which corresponds to N_{4d} was found to be 39 % for NbC. For the other species, the occupation was calculated with the same method.

Figure 2 and 3 show the relation between $L_{\gamma 1}/L_{\beta 1}$ and the 4d orbital occupation. It shows the $L_{\gamma 1}/L_{\beta 1}$ increasing linearly with an increase in the occupation in the niobium and molybdenum compounds, respectively. This feature accords with a trend expected from the formula expressed in Eq. (3), as the $L_{\gamma 1}$ intensity increases with an increase in the niobium 4d electron density (N_{4d}).

4. Acknowledgement

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Table 1. Calculation of molecular orbitals in NbC by the GAMESS MO method.

Molecular Orbital	Energy eV	Occupation / % Nb 4s	4p	4d	5s	C 2s	2p
$2t_{2g}$	- 7.71			39			61
$1t_{1g}$	- 9.20			37			63
$4e_g$	-10.21			7		15	78
$7a_{1g}$	-15.80	6		8	31	43	12
$5t_{1u}$	-19.18		1			99	
$3e_g$	-20.96				35	65	
$6a_{1g}$	-28.57				100		
$4t_{1u}$	-50.56		100				

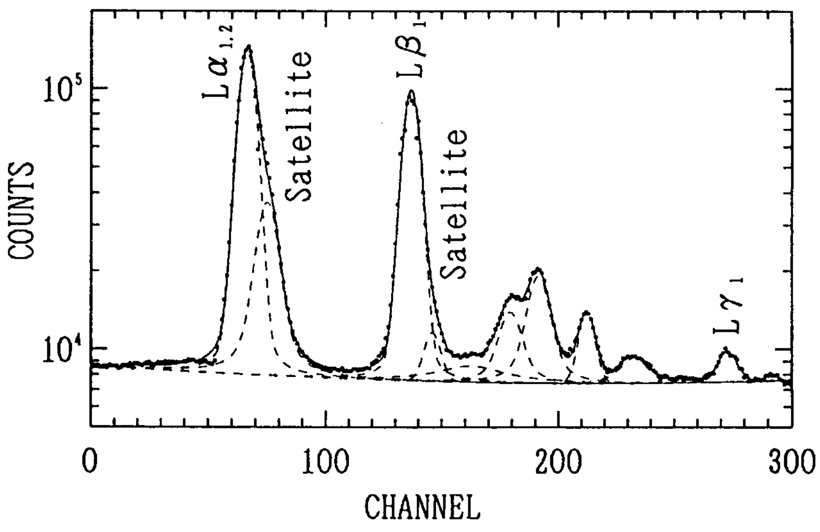

Fig. 1. Lx-ray spectrum of NbC excited by 11 keV electron beam.

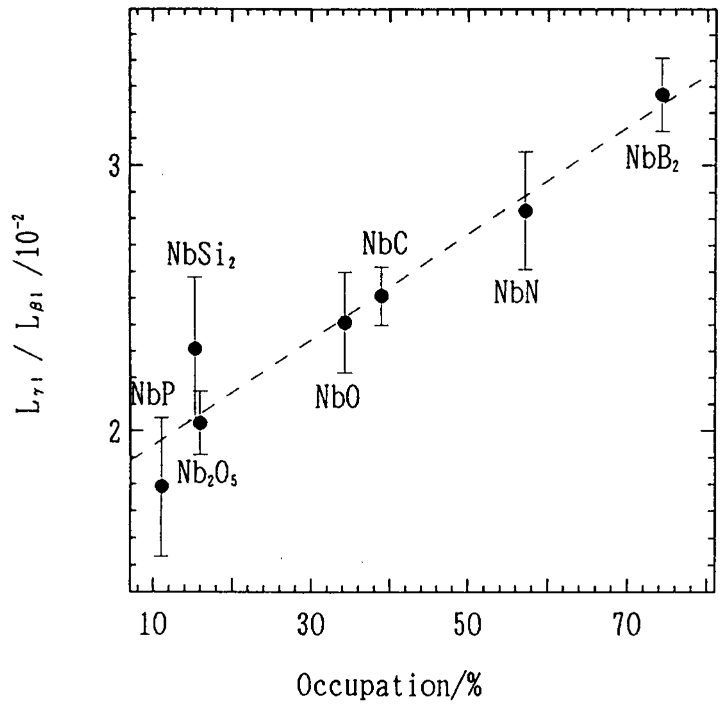

Fig. 2. Dependence of the $L_{\gamma 1}/L_{\beta 1}$ intensity ratio of niobium compounds on the niobium 4d occupation.

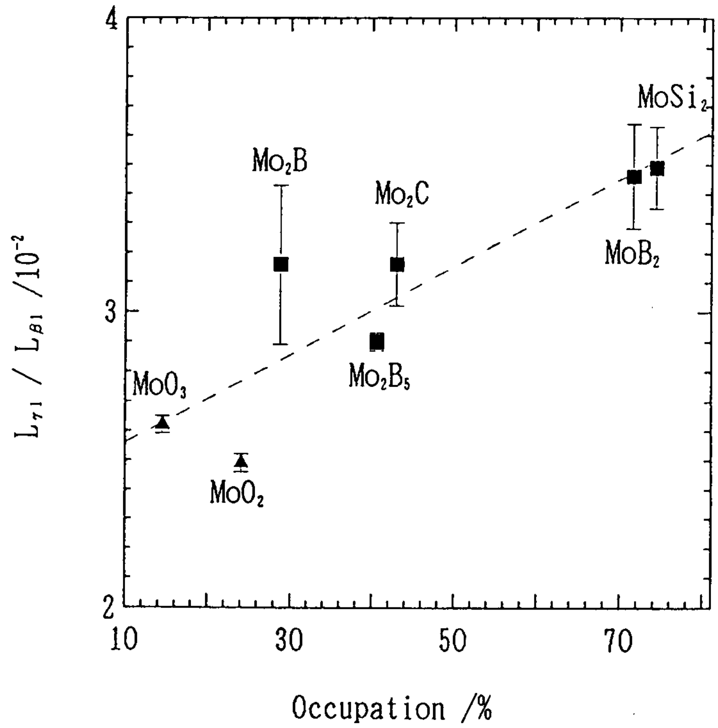

Fig. 3. Dependence of the $L_{\gamma 1}/L_{\beta 1}$ intensity ratio of molybdenum compounds on the molybdenum 4d occupation (■ : this work ▲: Fujiwara et al.[11]).