

Chemical Effects of L 1/L 1 X-Ray Intensity Ratio in Niobium Compounds

著者	Iihara J., Izawa G., Omori T., Yoshihara K.
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II. 4 Chemical Effects of $L_{\gamma 1}/L_{\beta 1}$ X-Ray Intensity Ratio in Niobium Compounds

Iihara J., Izawa G., Omori T. and Yoshihara K.
Department of Chemistry, Faculty of Science, Tohoku University

Introduction

X-rays emitted from atoms are affected by the chemical bonding of the atom.¹⁾ Especially, the transition of a valence shell electron to an inner shell vacancy causes a slight energy shift and a significant change in the X-ray spectrum. The X-ray intensity ratio affected by the chemical state of target materials has extensively been studied on the X-rays emitted from the decayed atom of radionuclides and also on X-ray induced by heavy ion bombardment. Though these excitation methods are quite different, the variation of X-ray intensity ratio by the chemical state can arise from the satellite lines in addition to the normal diagram lines. The direct observation of the satellite lines brings about the difficulties because of the weakness of satellite X-ray intensity and because of the required high resolution of a spectrometer. Consequently, the measurement of the ratio of the X-ray intensity method is adopted as a simple method in order to observe X-ray emission affected by the chemical state.

In this work, niobium L X-rays emitted from several niobium compounds which were excited with 3 MeV proton and 11 keV electron beams, were measured using a crystal X-ray spectrometer. Since $L_{\beta 1}$ comes from the transition between inner shells, ($L_{II}M_{IV}$), and $L_{\gamma 1}$ arises from the transition, ($L_{II}N_{IV}$), which directly relates to a valence shell electrons, the X-ray intensity ratio of $L_{\gamma 1}/L_{\beta 1}$ are appropriate to discuss in relation to the chemical state of niobium compounds.

Experimental

The chemicals used were $NbSi_2$, Nb_2O_5 , NbB_2 , NbC and niobium metal, of purity higher than 99.5 %, were purchased from the Mitsuwa Pure Chemicals and were used without further purification.

All the chemicals in powder form were copressed to discs of 0.1 mm in the thickness for the electron bombardment. Very thin targets were required, when these were bombarded with 3 MeV protons. Thus, the chemicals were ground finely less than 0.1 μm in diameter. The powders were mixed with 2 % CM cellulose. After lyophilization, the target was sliced to 40 μm in thickness. The microscopic observation showed that the particles of the chemicals were ground finely, but the chemicals were not distributed homogeneously in the CM cellulose matrix.

The X-ray spectra were measured using a Johansson-type curved-crystal spectrometer (size: 12.7 cm), Model ASM-SX designed by the Shimazu Seisakusho Co. Ltd. The spectra were obtained using an ADP crystal ($2d=1.0642$ nm), of which FWHM was 0.0011 nm at Mo L_{α} 0.5406 nm.

Results and Discussion

The lines of L_{η} , $L_{\alpha 1,2}$, $L_{\beta 1}$, $L_{\beta 3}$, $L_{\beta 4}$, $L_{\beta 6}$, $L_{\gamma 5}$ and $L_{\gamma 1}$ were observed in the spectra of niobium compounds by means of 11 keV electron beam and 3 MeV proton beam excitations. No substantial deformation of the peak shapes of $L_{\alpha 1,2}$ and $L_{\beta 1}$ was found.

The chemical effect related to the transition probability of valence shell electron may reflect in the intensity of $L_{\gamma 1}$. On the other hand, the intensity of $L_{\beta 1}$, which is the inner shell transition from M_{IV} level to L_{II} , seems not to vary by the chemical environment. Thus, the intensity ratios of $L_{\gamma 1}/L_{\beta 1}$ are compared in a series of niobium compounds. In order to assure this consideration, the ratios of $L_{\eta}/L_{\beta 1}$ were also obtained, where L_{η} X-rays is due to the inner shell transition from M_I to L_{II} .

The Pauling's ionicity is employed for the presentation of the correlation between X-ray intensity ratio of niobium compounds and its chemical state as mentioned in the previous paper.¹⁾ The relation between the X-ray intensity of $L_{\gamma 1}/L_{\beta 1}$ and the ionicity of niobium compounds obtained by the electron excitation is shown in Fig. 1, together with the intensity ratios of $L_{\eta}/L_{\beta 1}$. The intensity ratio of $L_{\gamma 1}/L_{\beta 1}$ decreases linearly with an increase in the ionicity. In the niobium compounds electrons of the outer most shells participate the formation of molecular orbitals with electrons of atoms bound to niobium. The electron distribution of valence shell of niobium atom decreases with an increase in the electron negativity of combined atom and consequently decreases with an increase of the ionicity of the compound.

The intensity ratio of $L_{\gamma 1}/L_{\beta 1}$ depends apparently on the chemical state of niobium compounds. On the contrary, the intensity ratio of $L_{\eta}/L_{\beta 1}$ is not affected by the chemical state of the compounds, though the statistics of the data is rather poor because of its small peak area.

The above consideration leads to the conclusion that the X-ray intensity is strongly related to the electron density. Thus, the electron density of valence shell is calculated in the niobium compound. From the relation between ionicity and $L_{\eta}/L_{\beta 1}$ X-ray intensity ratios, inner shells of niobium atom are not affected by the effect of chemical state resulting from chemical bonding. Since the extended Hückel molecular orbital calculation is concerned only to the interaction between outer shell orbitals, it is applicable to the calculation for the electron density of the niobium compounds. The calculation was performed in the range of one cluster around the central niobium atom. The occupation which is defined by the contribution ratio of an atomic orbital to a molecular orbital, was calculated on the basis of a coefficient of the atomic orbital which constructs the molecular orbital.

Since the intensity of $L_{\gamma 1}$ X-ray is considered to depend on the electron density of N_{IV} atomic level, the occupation is calculated from the coefficient of N_{IV} atomic level which is assigned to the molecular orbital of niobium compounds.

Figure 2 shows the relation between the $L_{\gamma 1}/L_{\beta 1}$ X-ray intensity ratio and the occupation of 4d orbital in the niobium compounds. The X-ray intensity ratio of $L_{\gamma 1}/L_{\beta 1}$ decreases with a decrease in the occupation of niobium compounds. This feature is similar to that in the ionicity. Accordingly, the occupation is reasonable term for the theoretical expression of chemical state of niobium atom.

In conclusion, the X-ray intensity ratios of $L_{\gamma 1}/L_{\beta 1}$ were measured for niobium compounds with 11 keV electron beam and 3 MeV proton beam. It is found that the X-ray intensity ratio of $L_{\gamma 1}/L_{\beta 1}$ decreases with an increase in the ionicity like as found in the molybdenum compound system. From the view point of theoretical consideration, the occupation may be introduced successfully to express the chemical state of niobium atom instead of the ionicity.

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Reference

- 1) Izawa G., Fujiwara H., Omori T. and Yoshihara K., CYRIC Annual Report 1986, p.141.

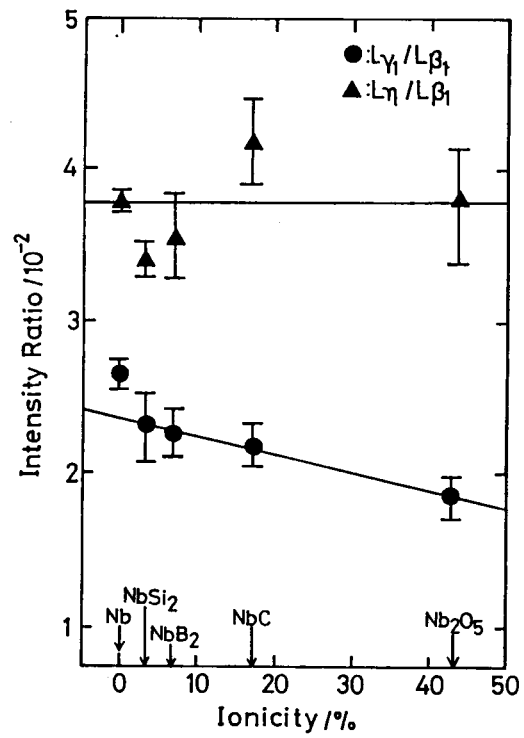


Fig. 1. Dependence of intensity ratio on the ionicity.

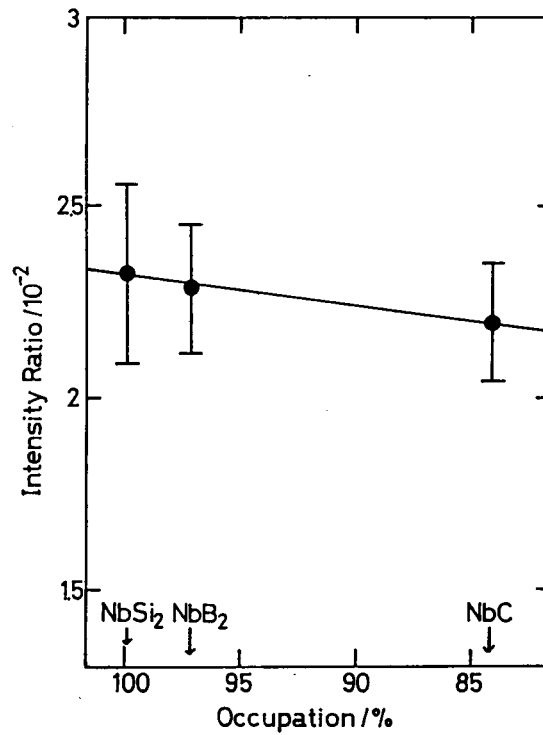


Fig. 2. Dependence of intensity ratio on the occupation.