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II. 1. Measurements of L x-Ray Chemical Influence in Chromium Compounds

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Introduction

The chemical effects on x-ray spectrum appear as change of peak energy, profile and intensity. We have studied the chemical effects on L x-rays of niobium and molybdenum compounds. We found the chemical effects of the L_{γ_1}/L_{β_1} intensity ratios in niobium and molybdenum compounds (Ref. 1). And the intensity ratio change was explained by the change of valence electron density. Very little knowledge of the effects is present on L x-rays of other elements.

In the present work, we measured chromium L and oxygen K_α x-rays with very low energy (about 500 eV) using a crystal spectrometer. Electron configuration of chromium is $[Ar]3d^5 4s^1$ and that of oxygen is $[He]2s^2 2p^2$. Chromium $L_{\alpha_{1,2}}$, L_{β_1} and oxygen K_α x-rays are emitted by transition of $L_{III}M_{IV,V}$, $L_{II}M_{IV}$ and $KL_{II,III}$, respectively. Since chromium and oxygen valence shells contain $M_{IV,V}$ and $L_{II,III}$ shell electrons, respectively. Chromium L and oxygen K_α x-rays are expected to be affected by the chemical environment of their chemical bond. We have found the effects in this paper.

Experiment

The x-rays of Cr_2O_3 and $K_2Cr_2O_7$ were measured by a Johansson-type crystal spectrometer with RAP (Rubidium Acid Phtalate) crystal (2d = 26.121Å). The purity of the samples is more than 99.5 %. Targets for irradiation were pressed into the form of disc (13 mm in diameter, and 0.5 mm in thickness). X-rays were detected with a gas flow type proportional counter(using PR10 gas). The pressure of the sample chamber was held lower than 10^{-5} torr. Excitation of inner shell electrons is conducted with a 11 keV electron beam using a R-HEED type electron gun. An electron beam current was monitored during wavelength scanning. Control of the spectrometer and data processing were carried out by using a PDP11/05 microcomputer.

Results and discussion

The measured spectra of chromium metal and chromium oxide (Cr_2O_3) are shown in Fig. 1 and 2, respectively. The energy of Chromiun L and oxygen K_α (524.9 eV) x-rays are very near and measured in the same spectra. The oxygen K_α x-ray peak in Fig.1 is supposed to be originated from oxygen molecule adsorbed on the surface of chromium metal. In the chromium L x-ray region there are two components in Fig. 1 and three components in Fig. 2. Two of these components are assigned to be $L_{\alpha_{1,2}}$ (572.8eV) and L_{β_1} (582.8eV) according to the x-ray energy table described in ref.2. Another peak which has the lowest energy is not listed on the table and we describe this peak as L_x in this report.

The chemical effects of these compounds are discussed as follows. One is the relation between the chromium L x-ray intensity and the oxygen K_α x-ray intensity. The other is the relation between respective components of the chromium L x-ray.

i) Relation between Cr L x-ray and O K_α x-ray

Intensity ratios of chromium L x-rays to oxygen K_α x-ray are shown in Table 1. The ratios in Cr_2O_3 will be larger than in $K_2Cr_2O_7$ without correction because of the difference of the oxygen/chromium atomic ratio. Therefore this correction was made using the atomic ratios, 3/2 for Cr_2O_3 and 7/2 for $K_2Cr_2O_7$. Cr L^{total} denotes total intensity of chromium L x-rays. Chromium 2p valence electrons are expected to be pulled to the oxygen atom strongly as the formal oxidation number of chromium atom increases. Therefore, the Cr L^{total}/O K_α intensity ratio increases against the increase of the formal oxidation number of the chromium, as expected.

ii) Intensity ratios in chromium L x-rays

$L_{\beta_1}/L_{\alpha_{1,2}}$ and $Lx/L_{\alpha_{1,2}}$ intensity ratios of chromium compounds are shown in Table 2. All the $L_{\alpha_{1,2}}$, L_{β_1} and L_x peaks are influenced due to the chemical states of chromium atom. The $L_{\beta_1}/L_{\alpha_{1,2}}$ and $L_x/L_{\alpha_{1,2}}$ intensity ratios are remarkably influenced by the chemical species. The tendency of the ratio change is that the $L_{\alpha_{1,2}}$ intensity of Cr_2O_3 is weaker than that of $K_2Cr_2O_7$ relatively. This result means that M_V shell electron density concerned with L_{α_1} is decreased.

References

1). Iihara J., et al., Nucl.Instr. Meth. A299 (1990) 394.
2). Bearden J. A., Rev. Mod. Phys., 39 (1967) 78.

Table 1. Cr L/O K_α x-ray intensity ratios.

	CrL^{total}/OK_α	$CrL_{\alpha1,\alpha2}/OK_\alpha$	$CrL_{\beta1}/OK_\alpha$	CrL_x/OK_α
Cr_2O_3	0.27	0.13	0.079	0.067
corrected	0.41	0.19	0.12	0.10
$K_2Cr_2O_7$	0.19	0.12	0.047	0.020
corrected	0.66	0.43	0.16	0.07
$K_2Cr_2O_7/Cr_2O_3$	1.6	2.3	1.3	0.70

Table 2. Chromium Lx-ray Intensity Ratios.

	$L_{\beta1}/L_{\alpha1,\alpha2}$	L_x/K_α
Cr_2O_3	0.64	0.52
$K_2Cr_2O_7$	0.38	0.16
Cr	0.18	

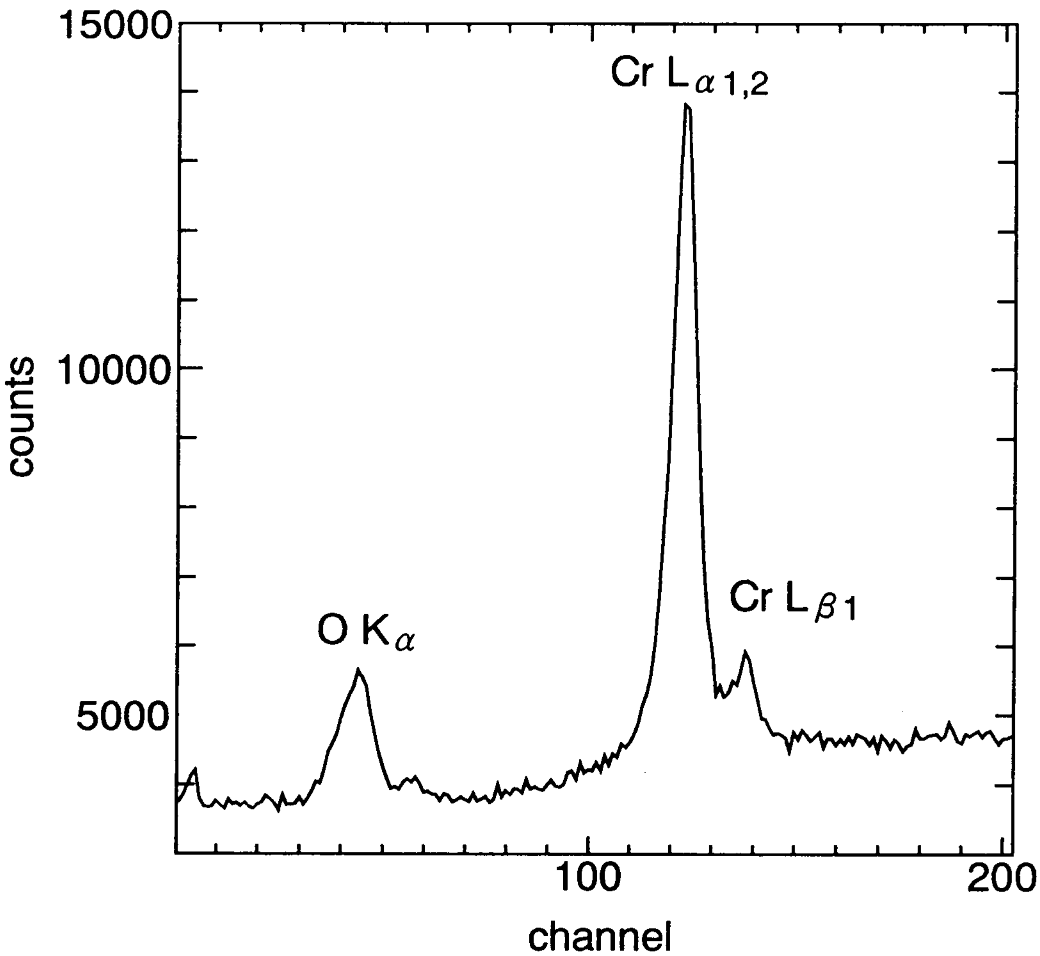

Fig. 1. X-ray spectrum of chromium metal.

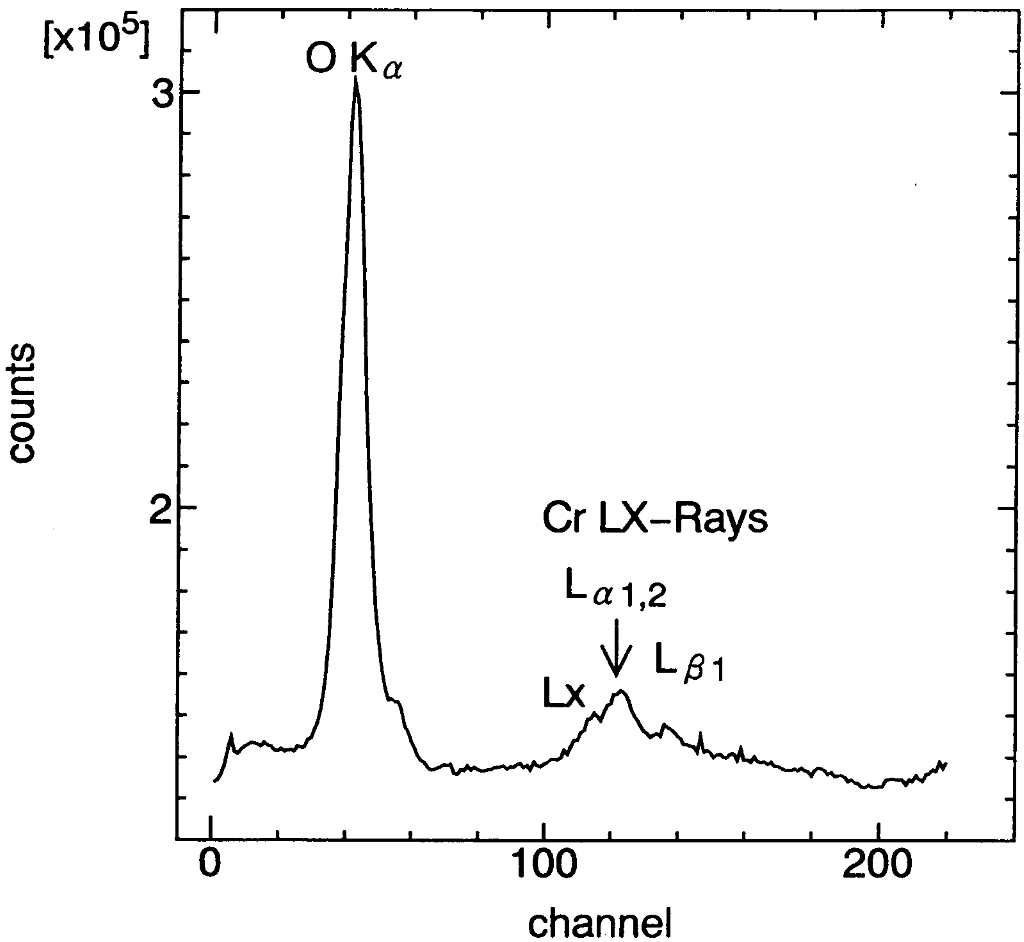

Fig. 2. X-ray spectrum of Cr_2O_3.