

# Chemical Effects in High-Resolution Nickel $K_{\alpha}$ X-Ray Fluorescence Spectra

Jun KAWAI,\* Michiharu OHTA,\* and Tokuzo KONISHI\*\*

\*Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

\*\*Analytical Research Laboratory, Asahi Chemical Industry, 2-1 Samejima, Fuji 416-8501, Japan

The nickel  $K_{\alpha}$  spectra of oxides, halides ( $\text{NiF}_2$ ,  $\text{K}_2\text{NiF}_6$ ,  $\text{NiCl}_2$ ,  $\text{NiBr}_2$ ), complex compounds, and metal are measured with two different double-crystal X-ray fluorescence spectrometers. The peak shifts and line width changes due to the changes in the chemical states are reported. High reproducibility has been shown for the chemical shift and line width measurements. The DV- $X\alpha$  molecular orbital calculation at the ground and the  $1s^{-1}$  hole states was performed to prove that the chemical effect originates from the charge-transfer mechanism.

(Received December 23, 2004; Accepted May 6, 2005)

## Introduction

Though X-ray fluorescence analysis is used for elemental analysis, high-resolution measurements with a double-crystal X-ray fluorescence spectrometer reveal a chemical shift of the characteristic X-ray lines owing to a change of the chemical environment.<sup>1</sup> Both the line width and the peak shift of the  $K_{\alpha 1}$  line are strongly correlated with the number of unpaired 3d electrons, or valency, and the ligands in the transition metal compounds.<sup>2,3</sup> The profile changes of the high-resolution  $K_{\alpha}$  X-ray fluorescence spectra due to the chemical states and their theoretical interpretations were reported for Sc,<sup>4</sup> Ti,<sup>5</sup> V,<sup>6</sup> Cr,<sup>7</sup> Mn,<sup>7</sup> Fe,<sup>8</sup> Co,<sup>9</sup> and Cu.<sup>10</sup> For Ni, the chemical effects on the line shape in high-resolution  $K_{\alpha}$  X-ray spectra were for only a few compounds,<sup>2,3,11-15</sup> but along with the development of rechargeable electric batteries, the number of reported compounds became large.<sup>16</sup> However, the interpretation of the line width has been different among researchers.

Tsutsumi<sup>17</sup> proposed an interpretation that the line width was proportional to the multiplicity,  $J(2S + 1)$ , of the 3d level, where  $J$  is the exchange integral. Then Kawai *et al.*<sup>18</sup> proposed a charge-transfer mechanism, where, in the  $1s^{-1}$  hole state, ligand 2p electrons were attracted by some of the Ni atoms and consequently the 3d holes were filled by the electrons transferred from a ligand (well-screened state), while the other Ni atoms do not attract any electrons from the ligand (poorly screened state) because of a too fast atomic process. As a consequence of these two processes, the X-ray peak was split into two peaks due to the presence or absence of the charge-transfer from the ligand, and became broader. As mentioned above, quite similar papers<sup>15,16</sup> on Ni measured by double-crystal spectrometers were published in the same issue of the journal, *X-Ray Spectrometry*, guest edited by one of the present authors. Konishi *et al.*<sup>16</sup> measured 32 nickel compounds, which were interpreted by Kawai's charge-transfer mechanism.<sup>18</sup> Shigemi *et al.*<sup>15</sup> measured two nickel compounds and a metal reference, which were interpreted by Tsutsumi's exchange splitting theory.<sup>17</sup> Because a paper that denies the editor's theory was published in the journal edited by the editor does not

mean that the editor has accepted the denial. It is the duty of the journal editor to open the door for various ways of discussion. The line broadenings of late transition-metal compounds, such as nickel and cobalt, are not remarkable compared with those of early transition metal compounds. This is well interpreted in such a way that Kawai's charge-transfer mechanism plays a major role for late transition-metal compounds, while Tsutsumi's exchange mechanism plays a major role for early transition-metal compounds.<sup>19</sup>

The purpose of the present paper is to show the reproducibility of Konishi's experiment in another type of spectrometer, as well as to prove the charge-transfer mechanism through a molecular orbital calculation.

## Experimental

The double-crystal spectrometers used had the following specifications.

(I) A high-resolution double-crystal X-ray fluorescence spectrometer fabricated by Rigaku Co. Ltd. (Spectrometer-I): The details of this spectrometer were described elsewhere.<sup>20</sup> The samples were excited by a W anode X-ray tube, the input power of which was 50 kV, 40 mA. The analyzing crystals were Si(220) + Si(220) ( $2d = 3.84 \text{ \AA}$ ). The step scan range was from 7450 to 7490 eV, and one step was typically 2 s. A gas flow proportional counter was used for X-ray detection. In what follows, we call this spectrometer Spectrometer-I. When the vacuum envelope temperature increased, the  $K_{\alpha}$  peak shifted, because the mechanical elements and the analyzing crystals in the spectrometer were thermally expanded. Therefore, the spectrometer temperature was stabilized within  $\pm 0.2$  degrees during the measurement. Figure 1 shows the good reproducibility of three successive measurements of  $\text{NiF}_2$ , from which the peak position and the line width were read, as shown in the figure. The open circles are measured raw data and the solid lines are smoothed spectra.

(II) A high-resolution double-crystal X-ray fluorescence spectrometer fabricated by Technos Co. Ltd. (Spectrometer-II): The mechanism of this spectrometer was essentially the same as

Table 1 The peak shift and FWHM of Ni  $K_{\alpha 1}$  peak measured with Spectrometers-I and II

Compound	Spectrometer-I		Spectrometer-II	
	Peak shift/eV	FWHM/eV	Peak shift/eV	FWHM/eV
$K_2NiF_6(IV)$	0.495 <sup>a</sup> ( $\pm 0.045$ ) <sup>b</sup>	3.491 ( $\pm 0.147$ )		
$Ni_2O_3(III)$	0.433 ( $\pm 0.031$ )	3.062 ( $\pm 0.124$ )		
NiPc	0.018 ( $\pm 0.040$ )	2.587 ( $\pm 0.073$ )		
Ni(salen)	0.133 ( $\pm 0.110$ )	2.455 ( $\pm 0.119$ )	0.021 ( $\pm 0.007$ )	2.442 ( $\pm 0.017$ )
$NiBr_2$	0.233 ( $\pm 0.022$ )	2.985 ( $\pm 0.035$ )	0.223 ( $\pm 0.010$ )	2.885 ( $\pm 0.010$ )
$NiCl_2$	0.268 ( $\pm 0.020$ )	3.039 ( $\pm 0.098$ )	0.263 ( $\pm 0.007$ )	2.878 ( $\pm 0.020$ )
NiO	0.377 ( $\pm 0.013$ )	2.980 ( $\pm 0.082$ )	0.357 ( $\pm 0.008$ )	2.802 ( $\pm 0.015$ )
$Ni(acac)_2$	0.397 ( $\pm 0.047$ )	3.147 ( $\pm 0.076$ )	0.384 ( $\pm 0.009$ )	3.051 ( $\pm 0.014$ )
$NiF_2$	0.521 ( $\pm 0.004$ )	3.357 ( $\pm 0.048$ )	0.502 ( $\pm 0.004$ )	3.261 ( $\pm 0.051$ )
Ni(metal)	0.00	2.384 ( $\pm 0.083$ )	0.00	2.315 ( $\pm 0.021$ )

a. Average of three measurements. b. Standard deviation  $\sigma_{n-1}$ .

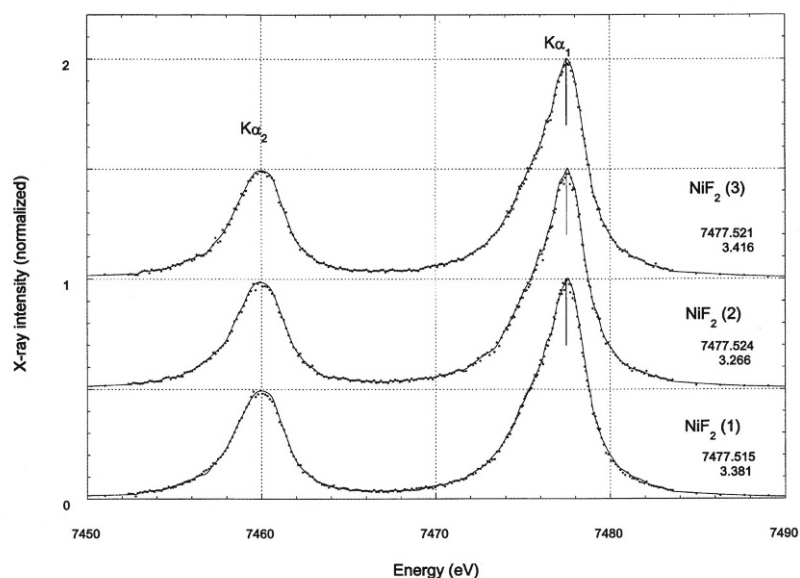


Fig. 1 Ni  $K_{\alpha}$  spectra of  $NiF_2$  measured with Spectrometer-I. Three successive measurements are plotted. Open circles, raw data; solid lines, smoothed. The peak energy and the FWHM are shown.

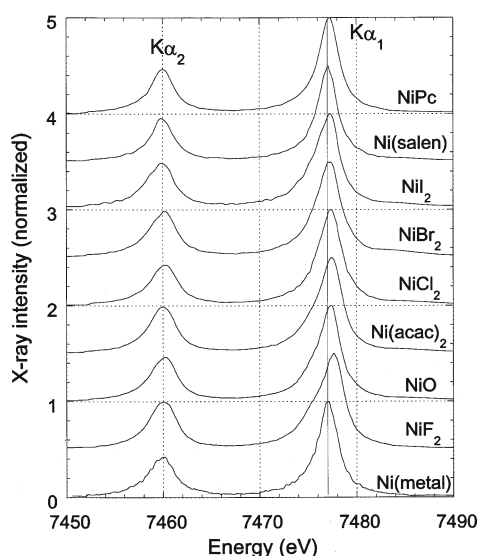


Fig. 2 Ni  $K_{\alpha}$  spectra of Ni (metal) and Ni compounds measured with Spectrometer-I. The spectra were normalized with respect to the peak maximum. The broken lines are the Ni  $K_{\alpha}$  spectra of Ni (metal).

that of the Rigaku one, and was published elsewhere.<sup>21</sup> The analyzing crystals were also Si(220) + Si(220). A rotating anode (W) tube (35 kV, 50–150 mA) was used and the maximum peak intensity was kept about 10000 cps. The spectrometer temperature was stabilized within  $\pm 0.1$  degrees during the whole measurement. The details of the experiment were similar to those described in Ref. 16.

The samples measured were high-spin Ni compounds: Ni halides ( $NiF_2$ ,  $NiCl_2$  and  $NiBr_2$ ) and Ni oxide, which were six-fold compounds, and the low-spin Ni compounds: Ni(salen) and Ni phthalocyanine (NiPc), which were the four-fold compounds. The structural formula of Ni(salen) is shown in Ref. 16.  $K_2NiF_6$  and  $Ni_2O_3$  were also measured. The purities of all the samples measured by Spectrometer-I were 99.9%, and most of the chemicals were purchased from Soekawa and Kanto Chemicals. Ni(salen) was synthesized by Prof. Miyamura, Tokyo University of Science. The samples measured by Spectrometer-II were the same as those reported in Ref. 16. Powder samples were pressed into briquettes; a metallic sample was measured as received.

To check the reproducibility, Ni compounds were measured at least three times with both spectrometers. To obtain reliable shift data, the strong  $K_{\alpha}$  line of metallic nickel was measured

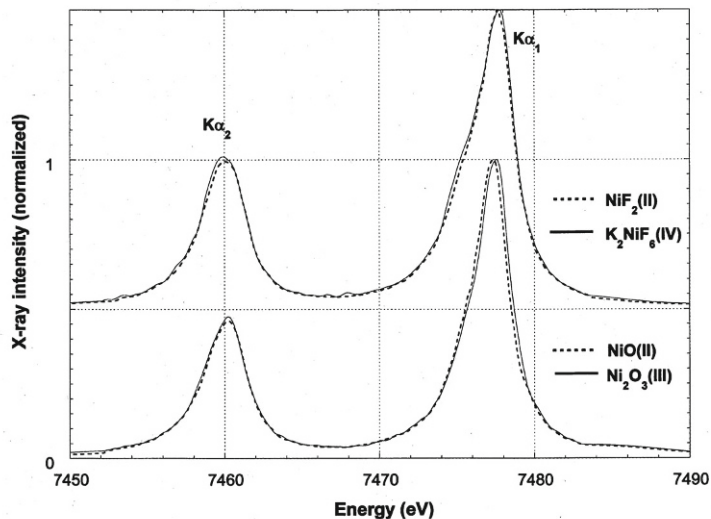


Fig. 3 Ni  $K_{\alpha}$  spectra of  $\text{NiF}_2$  and  $\text{K}_2\text{NiF}_6$  (top), and  $\text{NiO}$  and  $\text{Ni}_2\text{O}_3$  (bottom) measured with Spectrometer-I.

before and after the measurement of each nickel compound, the chemical shift of which was determined from the difference between the peak energy of the compound and the average peak energy of the nickel metal spectra measured before and after the compound.

## Results and Discussion

The X-ray fluorescence spectra of divalent Ni compounds measured with the spectrometer-I are shown in Fig. 2. These spectra were smoothed by the Savitzky-Golay method. In Fig. 2, the  $K_{\alpha 1}$  spectra of divalent nickel compounds,  $\text{Ni}(\text{salen})$  and  $\text{NiPc}$  were the low-spin compounds, and the other divalent compounds were high-spin, except for metal. These spectra were normalized with respect to the peak maximum. Compared with the  $K_{\alpha 1}$  peak of the metal, that of high-spin Ni compounds shifted to higher energy, and the peak shift ordering of  $K_{\alpha 1}$  was  $\text{NiBr}_2 < \text{NiCl}_2 < \text{NiO} < \text{Ni}(\text{acac})_2 < \text{NiF}_2$ . Oxygen atoms are six-fold coordinated in  $\text{Ni}(\text{acac})_2$ , and thus the local structure is similar to that of  $\text{NiO}$ . It is also found from Fig. 2 that the  $K_{\alpha 1}$  line widths of high-spin compounds are wider than that of low spin compounds. In particular, the FWHM of  $\text{NiF}_2$  is as wide as 3.3 eV, and that of the other high-spin Ni compounds are narrower (2.8–3.1 eV) than that of  $\text{NiF}_2$ . The  $K_{\alpha 1}$  peak shift as well as the FWHM measured with Spectrometers-I and II are given in Table 1. In spite of the fact that the peak shifts and line width were measured using two different spectrometers, the reproducibility is quite satisfactory, except for  $\text{Ni}(\text{salen})$ . This is probably due to the difference in the synthesis procedure; Spectrometer-I measured  $\text{Ni}(\text{salen})$  from Tokyo University of Science, while Spectrometer-II measured a sample from Fukuoka University.

When the peak intensity is weak, the standard deviation is large. The maximum peak intensity of the spectra measured with Spectrometer-II was twice or three times stronger than that of Spectrometer-I. Therefore, the deviation of the measured data obtained by Spectrometer-I was larger. This is the source of the larger standard deviations for Spectrometer-I than those of Spectrometer-II in Table 1.

The line shapes of  $K_{\alpha 1}$  are not symmetric.  $\text{NiF}_2$  and  $\text{NiO}$ , where the  $K_{\alpha 1}$  peak shifts are large, show prominent asymmetry.

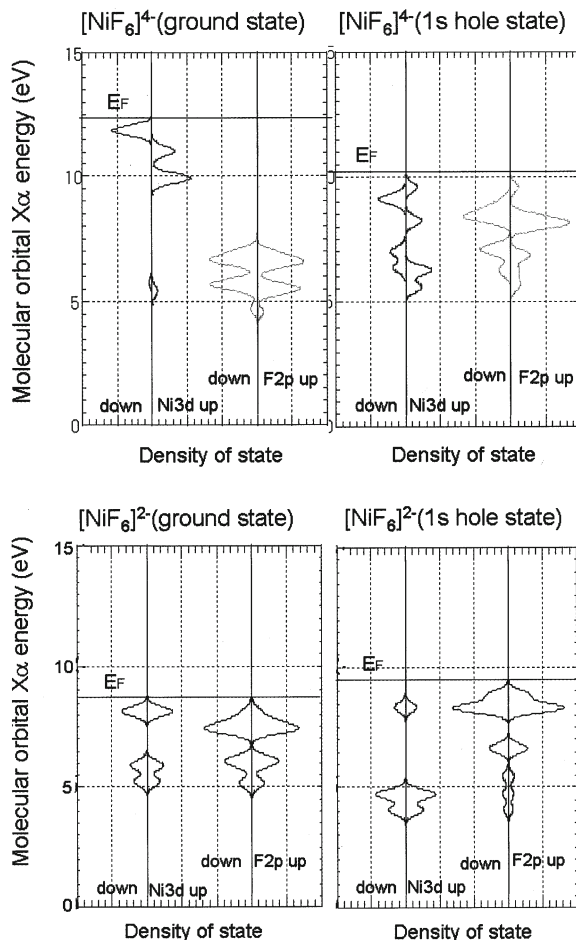


Fig. 4 Calculated electron density of states of Ni 3d and F 2p at the ground state (left) and the  $1s^{-1}$  hole state (right) for  $\text{NiF}_2$  (top) and  $\text{K}_2\text{NiF}_6$  (bottom). The Fermi energy ( $E_F$ ) is indicated by lines.

Kashiwakura and Gohshi<sup>12</sup> reported that the  $K_{\alpha 1}$  lines of  $\text{NiF}_2$  and  $\text{NiO}$  were separated into several peaks by the numerical deconvolution method.<sup>12</sup> The lower energy component of  $\text{NiF}_2$  and  $\text{NiO}$  is stronger than that of the other divalent Ni

compounds. This low-energy hump corresponds to the transition  $1s^{-1}3d^8 \longrightarrow 2p^{-1}3d^8$ , whereas the main peak corresponds to  $1s^{-1}3d^{9,10}\underline{L}^{1,2} \longrightarrow 2p^{-1}3d^{9,10}\underline{L}^{1,2}$ , where  $\underline{L}^{1,2}$  represents one or two hole(s) in the ligand orbital, after *e.g.* Bocquet *et al.*<sup>22</sup>

Figure 3 shows the difference between  $\text{NiF}_2$  and  $\text{K}_2\text{NiF}_6$ , as well as between  $\text{NiO}$  and  $\text{Ni}_2\text{O}_3$ . From the discussion of Konishi *et al.*,<sup>16</sup>  $\text{Ni}_2\text{O}_3$  is usually not a true  $\text{Ni}^{3+}$ , but a Ni defect structure, and Ni can be considered as  $\text{Ni}^{2+}$ . However, it is possible to find the chemical shift of  $\text{Ni}_2\text{O}_3$  from  $\text{NiO}$ . From a comparison of spectra between  $\text{NiF}_2$  and  $\text{K}_2\text{NiF}_6$ , the difference is not large, and thus the electronic structure is similar to each other from the view point of X-ray spectroscopy. We calculated the DV-X $\alpha$  electronic structure of the valence density of states for  $[\text{NiF}_6]^{4-}$  and  $[\text{NiF}_6]^{2-}$  as models of  $\text{NiF}_2$  and  $\text{K}_2\text{NiF}_6$ , respectively, as shown in Fig. 4. The calculational method was similar to those used in Ref. 19. The spin state of  $\text{K}_2\text{NiF}_6$  may change with the change of temperature; low spin for low temperature and high spin for high temperature. Because of the weak ligand field due to F,  $\text{K}_2\text{NiF}_6$  may be high spin at room temperature. However, at the  $1s^{-1}$  hole state, the density of states for both  $\text{NiF}_2$  and  $\text{K}_2\text{NiF}_6$  becomes similar as shown in Fig. 4, because of the charge transfer. In other words, the line shape of the  $\text{NiF}_2$  main peak, when the low-energy hump is neglected, is the line shape of the low-spin compounds. The Ni  $K_{\alpha 1}$  line width does not change remarkably compared with Ti, V, Cr, or Mn, of which the line width becomes twice when the compounds become low spin to high spin. The Ni  $K_{\alpha 1}$  line width merely increases from 2.5 (salen) to 3.3 eV ( $\text{NiF}_2$ ), *i.e.* 30% increase at  $\Delta S = 1$ . The Ti  $K_{\alpha 1}$  line width<sup>5</sup> increases from 1.4 ( $\text{TiB}_2$ ) to 2.2 eV [ $\text{Ti}_2(\text{SO}_4)_3$ ], *i.e.* 60% increase at  $\Delta S = 1/2$ .

## Conclusions

We measured the nickel  $K_{\alpha 1,2}$  X-ray fluorescence spectra of Ni compounds with two types of double-crystal X-ray fluorescence spectrometers. The reproducibility of the spectra was satisfactory. The small chemical effect compared with early transition metal compounds is due to the charge transfer effect at the moment of  $1s^{-1}$  hole creation.

## Acknowledgements

We thank Professor K. Miyamura (Tokyo University of Science) for providing us of the Ni(salen) complex. The present work was partially supported by Grant-in-Aid for Scientific Research, from the Ministry of Education, Science, and Culture, Japan.

## References

1. Y. Gohshi and A. Ohtsuka, *Spectrochim. Acta, Part B*, **1981**, 36, 763.
2. J. Finster, G. Leonhardt, and A. Meisel, *J. Phys. Colloq.*, **1971**, 32, C4-218.
3. A. Meisel, G. Leonhardt, and R. Szargan, "X-ray Spectra and Chemical Bonding", translated and edited by E. Källne and R. D. Deslattes, **1989**, Springer, Berlin, Heidelberg, 19.
4. J. Kawai, E. Nakamura, Y. Nihei, K. Fujisawa, and Y. Gohshi, *Spectrochim. Acta, Part B*, **1990**, 45, 463.
5. J. Kawai, T. Konishi, A. Shimohara, and Y. Gohshi, *Spectrochim. Acta, Part B*, **1994**, 49, 725.
6. Y. Gohshi, T. Nakamura, and M. Yoshimura, *X-ray Spectrom.*, **1975**, 4, 117.
7. Y. Gohshi and A. Ohtsuka, *Spectrochim. Acta, Part B*, **1973**, 28, 179.
8. J. Kawai, C. Suzuki, H. Adachi, T. Konishi, and Y. Gohshi, *Phys. Rev. B*, **1994**, 50, 11347.
9. C. Suzuki, J. Kawai, J. Tanizawa, H. Adachi, S. Kawasaki, M. Takano, and T. Mukoyama, *Chem. Phys.*, **1999**, 241, 17.
10. J. Kawai, Y. Nihei, M. Fujinami, Y. Higashi, S. Fukushima, and Y. Gohshi, *Solid State Commun.*, **1989**, 70, 567.
11. M. Pessa and R. Uusitalo, *Solid State Commun.*, **1973**, 13, 1703.
12. J. Kashiwakura and Y. Gohshi, *Spectrochim. Acta, Part B*, **1981**, 36, 625.
13. H. Sorum and J. Bremer, *J. Phys. F: Met. Phys.*, **1982**, 12, 2721.
14. K. Lawniczak-Jablonska and J. Auleytner, *J. Phys. F: Met. Phys.*, **1982**, 12, 2729.
15. A. Shigemi, T. Tochio, T. Ishizuka, N. Shigeoka, K. Ito, A.-M. Vlaicu, Y. Ito, T. Mukoyama, and Y. Gohshi, *X-Ray Spectrom.*, **1999**, 28, 478.
16. T. Konishi, J. Kawai, M. Fujiwara, T. Kurisaki, H. Wakita, and Y. Gohshi, *X-Ray Spectrom.*, **1999**, 28, 470.
17. K. Tsutsumi, *J. Phys. Soc. Jpn.*, **1959**, 14, 1696.
18. J. Kawai, M. Takami, and C. Satoko, *Phys. Rev. Lett.*, **1990**, 65, 2193.
19. C. Suzuki, J. Kawai, H. Adachi, and T. Mukoyama, *Chem. Phys.*, **1999**, 247, 453.
20. Y. Gohshi, H. Kamada, K. Kohra, T. Utaka, and T. Arai, *Appl. Spectrosc.*, **1982**, 36, 171.
21. T. Konishi, K. Nishihagi, and K. Taniguchi, *Rev. Sci. Instrum.*, **1991**, 62, 2588.
22. A. E. Bocquet, T. Mizokawa, T. Saito, H. Namatame, and A. Fujimori, *Phys. Rev. B*, **1991**, 46, 3771.