33. *Fine Structures in Sulfur and Iron X-Ray Emission Spectra*

By Yohichi GOHSHI and Hitoshi KAMADA

Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo

(Communicated by Takayuki SOMIYA, M. J. A., March 12, 1980)

Introduction. Recent advances in x-ray measurement techniques have made it possible to observe precisely x-ray spectra from various chemical compounds, materials for practical use and environmental samples. An x-ray spectrum shows small but clear chemical shifts or profile changes which reflect chemical states of atoms in matrix materials. Many works were reported to utilize this chemical effect for the characterization of materials by using so called "fingerprinting method". Theoretical efforts have been devoted to interpret various chemical effects in x-ray spectra. At present, however, mechanisms of these effects remain solved partly and still under theoretical research.

Considering this situation, the authors thought that high resolution spectra would give important informations for the interpretation of chemical effects in x-ray spectra. The effects are thought to be caused by line shifts and fine structures. A high resolution experiment will be useful to make these effects clearly observable. A difficulty, however, lies in this line of work. A natural width of an x-ray spectral line is broader than instrumental smearing due to spectrometer resolution. Most chemical effects are smaller than a natural width. Therefore, even with a very high resolution spectrometer it is not possible to resolve fine structures in x-ray spectra. This paper describes several results obtained by data processing developed by the authors and shows fine structures in x-ray spectra.

Experimental. Samples were excited with x-rays from a Cr (for S $K\beta$) or a W (for Fe $K\alpha$ and Mn $K\alpha$) target x-ray tube. Spectra were obtained through the single axis vacuum two-crystal spectrometer developed by the authors.¹⁾ Measuring conditions are given in Table I. Samples (α -S, α -Fe₂O₃, K₄Fe(CN)₆·3H₂O, K₃Fe(CN)₆, MnF₂, reagent grade) were pressed into a briquet and excited by x-rays under vacuum. Spectra were stored in a multichannel analyzer and accumulated repeatedly to improve counting statistics. The resultant spectra were fed into a computer and processed to elucidate fine structures.

Data processing. In general, a spectral line is broadened by a natural width (due to the Heisenberg's uncertainty principle), spectro-

Table I. Measuring conditions

X-ray	~40 kV, ~30 mA	Cr or W
Crystal	Ge $\begin{smallmatrix} (111) \times 2 \\ (220) \times 2 \end{smallmatrix}$	Si (111) $\times 2$
Slit (vertical)	1° or ~2°	
Spectrometer	Toshiba AFV 701 (prototype)	
X-ray path	Vacuum	

meter resolution, and energy level spread or splitting. The information of chemical interest mainly concerns the last two items (i.e. line position and its splitting). Instrumental resolution is often not significant, when a high resolution two-crystal spectrometer is used. Therefore, in x-ray wavelength region, a natural width of a spectral line is the most important factor of determining spectral line spread. Fortunately, line broadening due to a natural width is known to be expressed precisely by a Lorentzian function. To eliminate a broadening factor in spectral profile, a mathematical process called deconvolution is often adopted. There are several methods of deconvolution. Comparison of these methods will be found elsewhere.²⁾ The most practicable deconvolution process for a spectrum containing noise is the pseudo deconvolution proposed by van Cittert.⁴⁾ This method is rather resistant to noise which often becomes the cause of ringing in a processed spectrum. It, however, has the shortcoming that the convergence to the true solution is very slow. The improvement of the pseudo deconvolution was obtained by the authors.³⁾ The essential points are a) introduction of smoothing in the process of iterative calculation as shown in (1) and (2), and b) successive deconvolution.

$$\text{van Cittert} \quad G_n = G_{n-1} + [G_0 - G_{n-1} \otimes L] \quad (1)$$

$$\text{modified} \quad G_n = G_{n-1} + [G_0 - G_{n-1} \otimes L] \otimes S^{n-1} \quad (2)$$

G_0 : Original spectrum

L : Deconvolution function

S : Smoothing function

G_n : Deconvoluted spectrum after n iterations.

In Fig. 1, the original spectrum (top) was directly deconvoluted into the partly resolved spectrum (middle $l=1$). The improvement by smoothing is clearly shown, as no significant ringing due to noise appeared. The spectral lines in the middle spectrum, however, are not completely resolved. The effect of the successive deconvolution is found in the bottom spectrum ($l=4$). This method eliminate a natural width by a small increment. In this case, 1.4 eV FWHM Loretz function was decomposed into four 0.35 eV Lorentzian functions. The original spectrum was deconvoluted successively with 0.35 eV Lorentzian until the

total width of 1.4 eV deconvolution width was achieved. Resolution was enhanced appreciably without increasing riging or siderobe. This successive deconvolution was applied to the observed S $K\beta$ and Fe $K\alpha$ spectra.

Fig. 1. Mn $K\alpha$ from MnF_2 .

Results and discussion. *Valence band—Sulfur $K\beta$.* The valency electrons of sulfur are mainly 3p electrons. The electronic transition from 3p level to 1s hole (i.e. $K\beta$ emission) will reflect a valence band structure. A high resolution S $K\beta$ spectrum from α -S is shown in Fig. 2. The interpretation of this spectrum was given elsewhere.⁵⁾⁻⁸⁾ Although the profile indicates complicated structures, they are not resolved. After deconvolution of the natural width (0.45 eV) many

Fig. 2. High resolution S $K\beta$ spectrum.

Fig. 3. S $K\beta$ valence band spectrum after deconvolution.

structures are elucidated as shown in Fig. 3. A theoretical calculation of α -S band structure is indicated as vertical lines which are derived from the results by Salaneck *et al.*⁸⁾ A length of each line roughly corresponds to the intensity of each spectral line. Sulfur atoms in α -S form an eight membered puckered ring (S_8). The valence bands are grouped into 3p nonbonding (lone pair), 3p bonding (S-S σ bond), and very weak 3s bonding (S-S σ bond). Although correspondence of each group to the electronic energy levels (S $K\beta$) is rather excellent, the observed spectrum shows more complicated profile.

Fine structure—Fe $K\alpha$. It is well known that $K\alpha$ spectra of transition elements show profile changes depending on chemical states of x-ray emitting atoms. The change is rather small and only line broadening or asymmetry is observed. When the deconvolution of the natural width was applied, many fine structures were resolved as shown in Fig. 4. Nefedov proposed the multiplet splitting theory which correlate the splitting of $K\alpha_1$ and $K\alpha_2$ with the number of unpaired electrons.⁹⁾ In these spectra, $K_4Fe(CN)_6 \cdot 3H_2O$ has no unpaired electron ($n=0$) and shows very narrow single $K\alpha_1$ and $K\alpha_2$ lines as predicted by the Nefedov's theory. The other two compounds, $K_3Fe(CN)_6$ ($n=1$) and $\alpha-Fe_2O_3$ ($n=5$) are expected to have two $K\alpha_1$ + two $K\alpha_2$ lines and four $K\alpha_1$ + two $K\alpha_2$ lines, respectively. The spectra have more complicated structures especially in the $K\alpha_2$ region.

Conclusion. The high resolution x-ray emission spectra obtained with the deconvolution of the natural width were found to have various fine structures. High resolution S $K\beta$ for α -S, Fe $K\alpha$ for $K_4Fe(CN)_6 \cdot 3H_2O$, $K_3Fe(CN)_6$, and $\alpha-Fe_2O_3$ were presented. Comparison with the conventional theoretical calculation indicates that more sophisticated

Fig. 4. Fe K_{α} spectra.

approaches such as the $X\alpha$ method or the ligand field method with configuration interaction are needed in the analysis of the high resolution x-ray spectra from various compounds.¹⁰⁾⁻¹²⁾ This kind of analysis will be the basis of chemical state analysis by high resolution x-ray spectroscopy.

References

- 1) Y. Gohshi, Y. Hukao, and K. Hori: *Spectrochim. Acta*, **27B**, 135 (1972).
- 2) R. Chujo, Y. Gohshi, and K. Maeda: *J. Spectroscopical Soc. Japan*, **24**, 353 (1975).
- 3) J. Kashiwakura, and Y. Gohshi: *Spectrochim. Acta*, **30B**, 471 (1975).
- 4) H. Burger, and P. H. van Cittert: *Z. Physik.*, **79**, 722 (1932).
- 5) S. Ooba, S. Ueno, and Y. Gohshi: *J. American Ceram. Soc.*, **61**, 385 (1978).
- 6) H. C. Whitehead, and G. Andermann: *J. Phys. Chem.*, **77**, 721 (1973).
- 7) E. Kortela, E. Suoninen, M. Karras, and R. Manne: *J. Phys.*, ser. B, **5**, 2032 (1972).
- 8) W. R. Salaneck, N. O. Lipari, A. Paton, R. Zallen, and K. S. Liang: *Phys. Rev.*, **12**, 1493 (1975).
- 9) J. Finster, G. Leonhardt, and A. Meisel: *J. de Phys.*, **32**, C-4, 218 (1971).
- 10) A. Meisel: *Jpn. J. Appl. Phys.*, **17**, suppl. 2, 14 (1978).
- 11) S. Sugano: *Ibid.*, **17**, suppl. 2, 38 (1978).
- 12) R. Szargan, A. Meisel, E. Hartman, and G. Brunner: *Ibid.*, **17**, suppl. 2, 174 (1978).