Advanced Research Center for Beam Science
– Atomic and Molecular Structures –

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Scope of Research

Our laboratory analyzes the electronic state of atomic or molecular structure in materials, which are obtained from diffraction and spectra observed by X-ray irradiation, respectively, to elucidate the relationships between the structure and the physical properties. Our main themes are (1) high-resolution experimental and theoretical studies on the natural linewidth of elements in materials, (2) the development of the spectrometer in the measurements of the diagram lines in soft X-rays region, and (3) structural determination of novel protein molecules and their complexes.

KEYWORDS

High Resolution X-ray Crystal Spectrometer
Natural Linewidth
Chemical Shift
Structural Biology
Protein Crystallography
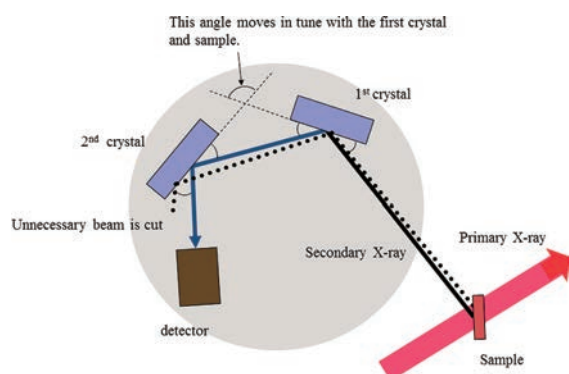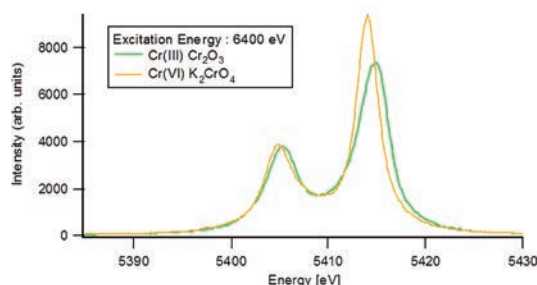
Selected Publications

Menesguen, Y.; Lepy, M.-C.; Honicke, P.; Muller, M.; Unterumsberger, R.; Beckoff, B.; Hoszowska, J.; Dousse, J.-Cl.; Blachucki, W.; Ito, Y.; Yamashita, M.; Fukushima, S., Experimental Determination of X-ray Atomic Fundamental Parameters of Nickel, *Metrologia*, **55,** 56 (2018).

Tanikawa, T.; Ito, Y.; Fukushima, S.; Yamashita, M.; Sugiyama, A.; Mizoguchi, T.; Okamoto, T.; Hirano, Y., Calcium is Cycled Tightly in Cryptomeria japonica Stands on Soils with Low Acid Buffering Capacity, *For. Ecol. Manage.*, **399,** 64-73 (2017).

Ito, Y.; Tochio, T.; Ohashi, H.; Yamashita, M.; Fukushima, S.; Polasik, M.; Slabkowska, K.; Syrocki, L.; Szymanska, E.; Rzadkiewicz, J.; Indelicato, P.; Marques, J. P.; Martins, M. C.; Santos, J. P.; Parente, F., $K\alpha_{1,2}$ X-ray Linewidths, Asymmetry Indecies, and [*KM*] Shake Probabilities in Elements Ca to Ge and Comparison with Theory for Ca, Ti, and Ge, *Phys. Rev.*, **A94,** 42506~1-11 (2016).

Ito, Y.; Tochio, T.; Fukushima, S.; Taborda, A.; Sampaio, J. M.; Marques, J. P.; Parente, F.; Indelicato, P.; Santos, J. P., Experimental and Theoretical Determination of the $K\alpha_2/K\alpha_1$ Intensity Ratio for Zinc, *J. quant. Spectrosc. Radiat. Transfer*, **151,** 295-299 (2015).

Fujii, T.; Sato, A.; Okamoto, Y.; Yamauchi, T.; Kato, S.; Yoshida, M.; Oikawa, T.; Hata, Y., The Crystal Structure of Maleylacetate Reductase from *Rhizobium* sp. strain MTP-10005 Provides Insights into the Reaction Mechanism of Enzymes in Its Original Family, *Proteins: Structure, Function, and Bioinformatics*, **84,** 1029-1042 (2016).

Fujii, T.; Yamauchi, T.; Ishiyama, M.; Gogami, Y.; Oikawa, T.; Hata, Y., Crystallographic Studies of Aspartate Racemase from *Lactobacillus sakei* NBRC 15893, *Acta Crystallogr. Sect. F Struct. Biol. Cryst. Commun.*, **71,** 1012-1016 (2015).

## $K\alpha_{1,2}$ X-ray Linewidths, Asymmetry Indices, and [*KM*] Shake Probabilities in Elements Ca to Ge

The content described below is the result of our research on the asymmetry of the $K\alpha_{1,2}$ x-ray spectra in the 3*d* transition metals that have been unknown in the history of about 100 years in atomic physics.

Research on the width and shape of the asymmetric $K\alpha$ x-ray doublet of 3*d* elements ($21 \leq Z \leq 30$) has been the object of interest for a long time, both from the theoretical and experimental points of view. Although several causes have been proposed to explain this asymmetry such as, for example, shake processes, conduction-band collective excitations, exchange, and final-state interactions, the origin of the asymmetric shape is still under investigation and debate.

In order to obtain a simple description of the Cu $K\alpha_{1,2}$ spectrum, Berger assumed a doublet model for each of the $K\alpha_1$ and $K\alpha_2$ peaks and used two pairs of Lorentzian functions, determined $K\alpha_{11}$ and $K\alpha_{12}$, and $K\alpha_{21}$ and $K\alpha_{22}$, respectively, to fit them. A physical meaning for this simple model was given by Deutsch et al., based on the theoretical reasoning that the asymmetry in Cu $K\alpha$ spectra is due to the existence of shake processes leading to a 3*d* spectator hole. When a hole is created in the 1*s* shell, there is a probability that a second hole is created also in the 3*d* subshell. This shake-off process leaves the system with two holes and will be referred to subsequently as [1*s*3*d*] shake. Thus, the $K\alpha_{11}$ and $K\alpha_{21}$ Lorentzian peaks would correspond to the $K\alpha_1$ and $K\alpha_2$ diagram lines, respectively, and the $K\alpha_{21}$ and $K\alpha_{22}$ peaks to the corresponding satellite lines.

In a similar way, Ito et al. attributed the asymmetry in Zn $K\alpha_{1,2}$ spectra to the [1*s*3*d*] shake processes. Using the two-Lorentzian model, Ito et al. and Polasik et al. investigated the emission line shape in elements Ti to Zn and concluded that the full width at half maximum (FWHM) of the $K\alpha_{11}$ line is larger in these elements than the semi-empirical values reported by Krause and Oliver.

As it was considered that a simple description of the peak profiles by two Lorentzian functions was acceptable for the Cu $K\alpha$ lines, we measured and analyzed systematically the $K\alpha$ emission spectra in elements from Ca to Ge using a high-resolution double-crystal x-ray spectrometer and the same model, in order to elucidate the physical meaning of the asymmetry index of the lines, and the contribution of the [*KM*] shake processes (Figure 1). The overall tendency of the corrected full width at half maximum of the $K\alpha_1$ and $K\alpha_2$ lines as a function of Z, as well as the linewidths, are in good agreement with the data reported in the literature (Figures 2 and 3). The asymmetry index of $K\alpha_1$ in 3d elements from Sc to Zn is ascribed to the existence of a 3*d* spectator hole (Figure 1).
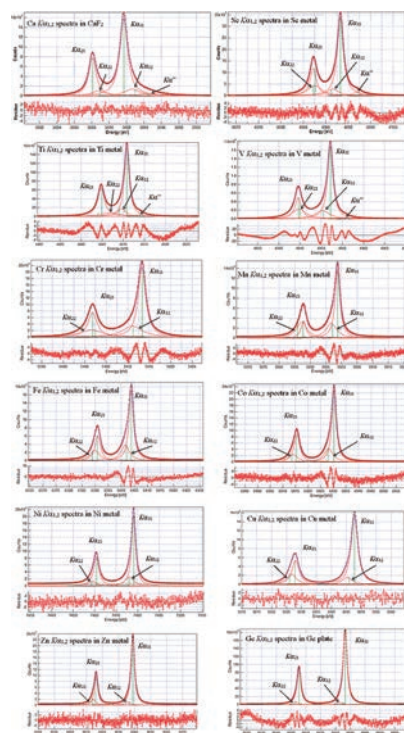
Figure 1. The observed $K\alpha_{1,2}$ spectra in elements Ca to Ge are shown with the Lorentzian functions used in the fitting process. These spectra were measured using the antiparallel double-crystal x-ray spectrometer. $K\alpha_{11}$ is the $K\alpha_1$ diagram line, and $K\alpha_{21}$ is the $K\alpha_2$ line. $K\alpha_{12}$ and $K\alpha_{22}$ satellite lines are due to $2p \rightarrow 1s$ electron transitions in the presence of an extra 3d hole resulting from shake processes. The $K\alpha$" line is a satellite line ascribed to a 3*p* spectator hole.
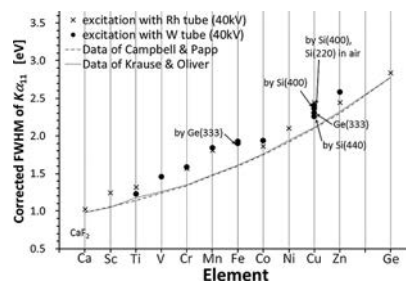
Figure 2. The corrected FWHM (CF) of the $K\alpha_{11}$ line of elements Ca to Ge together with the semi-empirical and recommended values. The widths of Krause and Oliver are semi-empirical values and those reported by Campbell and Papp are recommended values. The CF values for both the $K\alpha_{11}$ and $K\alpha_{21}$ diagram lines were obtained from the observed FWHM through Tochio's method.
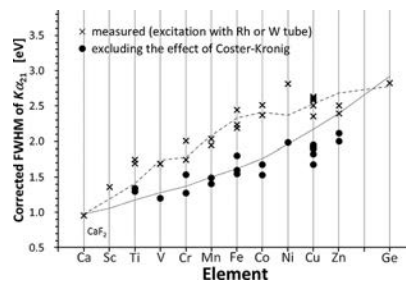
Figure 3. The CF of the $K\alpha_{21}$ line of elements Ca to Ge is shown together with the recommended values. Solid circles are the values subtracting the Coster-Kronig broadening effects reported by Nyholm *et al.*.