Developments of Lifetime-broadening-removed XANES Spectroscopy

X-ray absorption near-edge structure (XANES) is a powerful technique for studying electronic states around selected atomic species. XANES features are, however, often smeared out because of the natural lifetime width of the core holes. Intense monochromatic X-rays available at SPring-8 have made it possible to experimentally substantiate the observation of lifetime-broadening-removed (LBR) XANES from resonant inelastic X-ray scattering (RIXS) spectra [1]. In this article using CuO data it is demonstrated that 1*s*-LBR-XANES and 1*s* as well as 2*p*-LBR or lifetime-broadening-free (LBF) XANES can be deduced from experimental RIXS spectra.

The experiments were carried out at beamline **BL47XU**. The RIXS from powder CuO was analyzed with a spherically bent ϕ75 mm Si(444) crystal having an 820 mm radius of curvature, and detected by a scintillation counter. The overall resolution was 1.1 eV.

Figure 1 shows the excitation energy dependence of 1*s* 2*p* RIXS spectra of CuO [1]. Spectral shape and intensity change with excitation energy significantly. Excitation with X-ray energies well above the *K*-absorption edge energy yields a single band, which is the well-known Cu $K\alpha_1$. As the excitation energy is decreased, the main feature corresponding to the $K\alpha_1$ (A) is shifted down with its width broadened. By decreasing the excitation energy to ~ 8983 eV, a new branch (B) appears. Another feature labeled C is prominent at the excitation energy below 8983 eV, and is the strongest at the $1s \rightarrow 3d$ transition energy, ~ 8980 eV [2].

The differential cross section of 1*s* 2*p* RIXS process can be deduced from the well-known Kramers-Heisenberg equation [1,3]:

$$\frac{d\sigma(\omega_1)}{d\omega_2} \propto \int \frac{(\omega_2/\omega_1)(\Omega_{1s}+\omega)(dg_{1s}/d\omega)}{((\Omega_{1s}+\omega-\omega_1)^2+\Gamma_{1s}^2/4\hbar^2)((\Omega_{2p}+\omega_2+\omega-\omega_1)^2+\Gamma_{2p}^2/4\hbar^2)} d\omega \quad (1)$$

Here, $\hbar\omega_1$ and $\hbar\omega_2$ are incident and scattered photon energies, $\hbar\omega$ is the energy of the excited electron, and Γ_{1s} and Γ_{2p} are the widths of the 1*s* and 2*p* levels, the energies of which are represented by $\hbar\Omega_{1s}$ and $\hbar\Omega_{2p}$, respectively. The $dg_{1s}/d\omega$ corresponds to LBF-XANES profile.

Under the approximation that $\Gamma_{2p}/\hbar << 1$, Eq. (1) can be transformed in to Eq. (2) [1,3]:

$$\frac{d\sigma(\omega_1)}{d\omega_2} \propto \frac{(\omega_2/\omega_1)\,\omega_{abs}(dg_{1s}/d\omega_{abs})}{(\Omega_{1s}-\Omega_{2p}-\omega_2)^2+\Gamma_{1s}^2/4\hbar^2}, \quad (2)$$

where $\omega_{abs} = \Omega_{1s}+\omega$. Equation (2) allows us to calculate $dg_{1s}/d\omega$ analytically from the experimental RIXS spectra directly. The $dg_{1s}/d\omega$ derived (LBR-XANES) is free from the Γ_{1s} broadening and the width is determined only by Γ_{2p}.

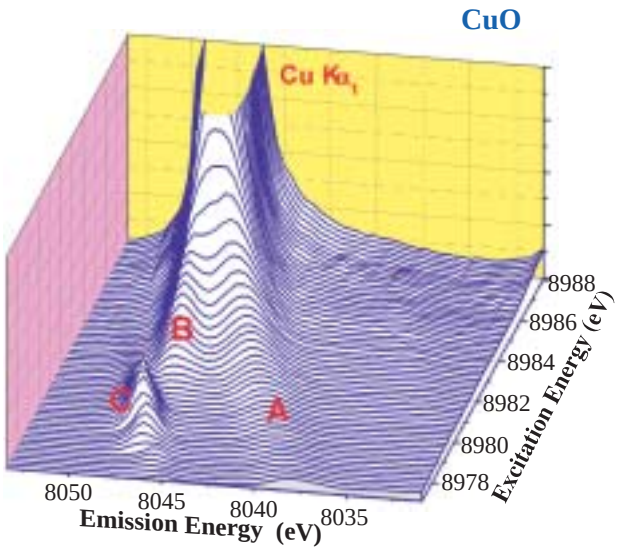

Fig. 1. Excitation energy dependence of RIXS spectra of CuO as a function of excitation energy and emission energy.

In the upper panel of Fig. 2, the RIXS spectra of CuO excited at several energies ('Exp.') are shown. The LBR-XANES profiles analytically derived from them are plotted in the lower panel. The inset shows $1s \rightarrow 3d$ transition region in an expanded scale. It is notable that, despite of significant differences in RIXS

spectra, the LBR-XANES derived almost overlaps with each other. Thus, complicated RIXS behavior can be fully explained as the reflection of the LBR-XANES: the RIXS features, A, B, and C, are determined by the XANES features, a, b, and c, respectively [1]. The LBR-XANES is much more distinct than conventional XANES, which suggests that Γ_{1s} broadening is removed.

Since the quality of the present RIXS data allows us to examine the profiles in detail numerically, deriving $dg_{1s}/d\omega$ on the basis of Eq. (1) without assuming $\Gamma_{2p}/\hbar << 1$ was attempted next. The $dg_{1s}/d\omega$ thus obtained corresponds to LBF-XANES. The $dg_{1s}/d\omega$ that reproduces the observed RIXS spectra best and the calculated RIXS profiles ('Best-fit LBF-XANES') are shown in the lower and the upper panels of Fig. 2, respectively. In the upper panel, it is found that the observed RIXS spectra almost exactly coincide with the calculations by the best-fit $dg_{1s}/d\omega$. In the lower panel, it is evident that the best-fit $dg_{1s}/d\omega$ shows much more distinct features than those analytically obtained, demonstrating that the lifetimes of 2p as well as 1s are removed.

Many exciting applications of the LBR- or LBF-XANES spectroscopy, e.g., for high-Tc materials [4], can be envisaged.

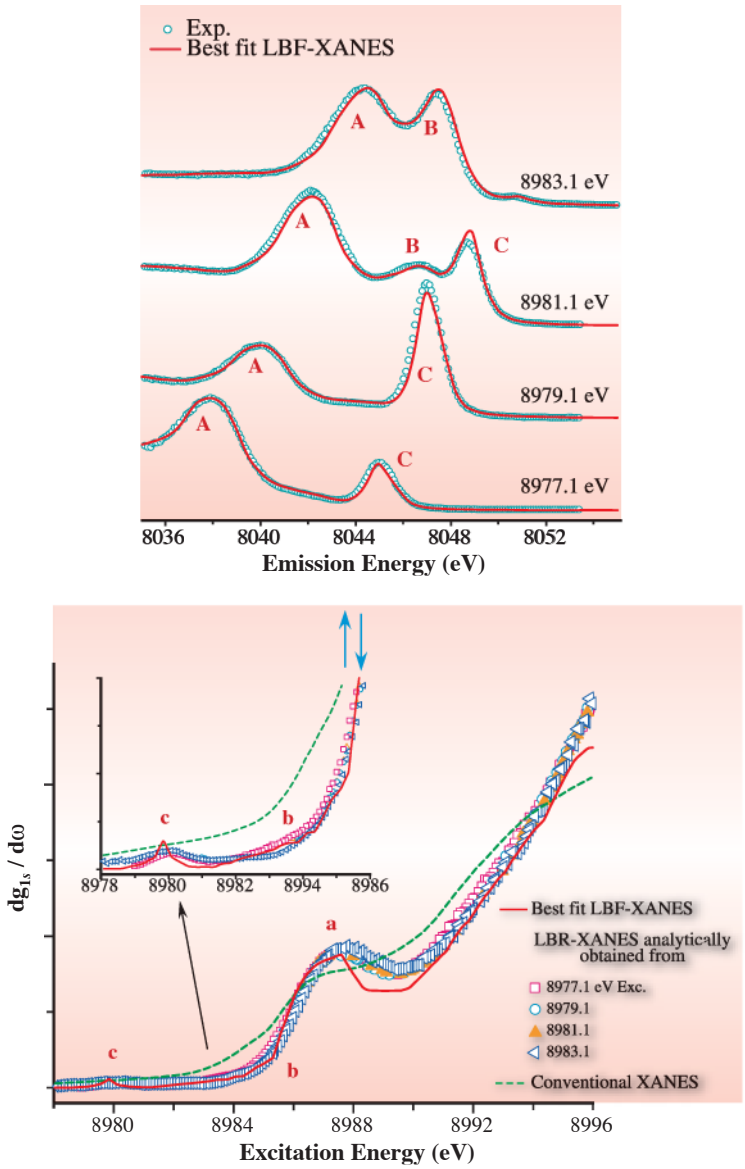

Fig. 2. Upper panel: comparisons of the observed RIXS spectra (circles) and calculated ones (solid line) using the best-fit $dg_{1s}/d\omega$ model. Lower panel: the best-fit LBF-XANES ($dg_{1s}/d\omega$) numerically obtained as well as LBR-XANES spectra analytically obtained from RIXS spectra of the upper panel. Conventional XANES is also shown for comparison.

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References

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