

Feature Article

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Development of New X-Ray Spectroscopy using Resonant Inelastic X-Ray Scattering

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We developed a method of determining the X-ray absorption fine structure (XAFS) spectrum through high-accuracy measurement of resonant inelastic X-ray scattering, without any limits on resolution of the inner-shell lifetime broadening. From this method, we can derive various new types of XAFS, including the valence selective XAFS and the spin selective XAFS (both without any limits of lifetime broadening). The method shows a possibility of developing into a powerful tool to monitor various condition changes for general functional materials.

Introduction

Most of you may have an image of X-ray fluorescence as having a peaked spectrum, with its energy position varying according to element. However, this image is not necessarily correct. "Strange X-ray fluorescence" is observed when a monochromatic X-ray having absorption edge energy, which is the lowest energy to enable inner-shell to excite, irradiates. The X-ray emission shows complex changes as described later, depending on a little difference of excitation energy. This study is an acrobatic one that focuses on the close relationship between this "strange X-ray fluorescence" and the absorption spectrum, and aims at applying this relationship to the measurement of "the next-generation absorption."

Background and History of Development

More than 30 years have passed since the rebirth of X-ray absorption spectroscopy as X-ray absorption fine structure (XAFS) spectroscopy, resulting from the advent of synchrotron radiation. At present, the XAFS method has been established as an element-selective analysis method for local structures and electron conditions, mainly with amorphous materials and liquids. However, the XAFS method has disadvantages. One of them is that the resolution is limited by the inner-shell lifetime broadening, which is dependent on the atomic number,

and limited from 1 eV (vanadium) to 40 eV (tungsten) in K shell^[1]. Accordingly, a chemical shift within the lifetime broadening cannot be separated, regardless of how measurement technology makes advances. That is why we only get averaged information in case that a sample contains the same element in different conditions regarding valence, spin, etc. or the reason of other restrictions such as the inability to observe the existence of small energy dispersion occurred due to decreased symmetry, which often provide important information on structure.

X-ray emission, observed in the excitation produced by energy near the absorption edge, is not a normal X-ray fluorescence created in the primary optical process; rather, it should be regarded as a resonant inelastic (Raman) X-ray scattering created in the secondary process. Accordingly, the analysis of the X-ray emission using the Kramers-Heisenberg formula (basic formula for the secondary process) should provide an "XAFS spectrum that is beyond limitations from the lifetime broadening (or lifetime broadening-suppressed)." I conceived this idea in the autumn of 2000. At that time, there was no environment for experiment in Japan where I could verify this idea. And therefore, I submitted my proposal to the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory, USA, and, simultaneously, applied for the position of the short-term research personnel at the Ministry of Education, Culture,

Sports, Science and Technology. Fortunately, both my proposal and application were accepted and I could conduct an experiment in the autumn of 2001 for one month, and got a result that backed my prediction. That is why results of my first two reports^[2, 3] in this study were obtained at the beam line X21 in NSLS.

Later, by utilizing research subsidies such as Grand-in-Aid for Scientific Research for young researchers (A) and from “PRESTO” (Japan Science and Technology Agency), I manufactured an X-ray spectrometer with large acceptance^[4] on my own from the design stage, and brought the system to SPring-8, a synchrotron radiation facility to realize X-ray emission measurement in the world-best sensitivity and also high resolution. Meanwhile, I also engaged in the improvement of the analysis method and established measurement and analysis methods for “the lifetime broadening-suppressed XAFS spectrum.” Furthermore, my studies paved the way to deriving “the lifetime broadening-suppressed spin selection XAFS^[5, 6]” and “the lifetime broadening-suppressed valence selection XAFS^[6, 7].” In the following sections, I will discuss, in detail, the relationship between the resonant inelastic X-ray scattering and the lifetime broadening-suppressed XAFS spectrum as the essence of the spectroscopy and the spectrum analysis method based on this relationship.

Resonant Inelastic X-Ray Scattering and Lifetime Broadening-Suppressed XAFS Spectrum

This article covers a process, illustrated in Figure 1(a), in which the electron 1s absorbs an X-ray photon with energy of ω_1 (in this article, the energy is represented as angular frequency ω); the resulting vacancy is filled with the electron 2p and a photon with energy of ω_2 is created. If the excitation energy is sufficiently high, this process results in normal $K\alpha$ fluorescence. In this process, if the excitation energy is near the absorption edge, the absorption and the emission should not be treated as two individual events, but as a single group of events of resonance inelastic scattering. Assuming this, the Kramers-Heisenberg formula can be applied to this process as a secondary process, as in the case of the Raman scattering of a visible light. The processes for the $K\beta$ or L emission are in the same way, too. If this formula is applied to the process in Figure 1 to take out its main part, when excited with an X-ray of ω_1 , the dependence of the scattering intensity, on ω_2 ; i.e. the inelastic scattering spectrum $d\sigma(\omega_1)/d\omega_2$ can be represented by Formula (1)^[3, 8-10].

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

The integrand in Formula (1) essentially consists of three functions combined, which have the energy ω of the excited electron in Figure 1(a) as the common variable (Figure 1 (b)). The first function is a Lorentz function that peaks at $\omega_1 - \Omega_{1s}$, with the lifetime broadening of the 1s vacancy (Γ_{1s}), occurring in the intermediate step, as full width at half maximum (f_1 , the first term of the denominator of Formula (1); the resolution of the normal absorption spectrum is limited with this width). The second function is another Lorentz function that peaks at $\omega_1 - \omega_2 - \Omega_{2p}$, with the lifetime broadening (Γ_{2p}) in the final step (f_2 , the second term of the denominator of Formula (1)). The third function is the oscillator strength distribution $dg_{1s}/d\omega$ proper to a given substance, that represents the high resolution XAFS which is not limited by the lifetime broadening (Γ_{1s}).

Observing the resonant inelastic scattering spectrum means measuring with the three combined functions as a function of the scattered light’s energy ω_2 , by moving f_2 in Figure 1(b), assuming f_1 (with a fixed ω_1 and an Ω_{1s} proper to a given substance) and $dg_{1s}/d\omega$ to be constant. The bottom of the Lorentz function f_1 can be regarded as mostly constant under the complete inelastic condition $\omega_1 - \Omega_{1s} \ll 0$. Accordingly, the scattering spectrum is determined as $dg_{1s}/d\omega$ convoluted with f_2 of a small breath, enabling the measurement of $dg_{1s}/d\omega$ with a high resolution. Regrettably, however, this method cannot be applied to a wide range of cases, because the spectrum is far from the resonance condition and that leads to the low intensity.

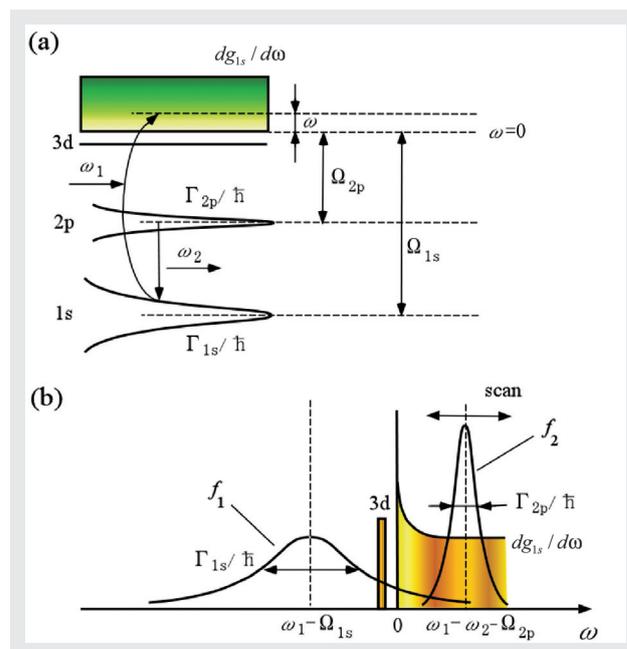


Figure 1 Illustrations of resonant inelastic X-ray scattering and the lifetime broadening-suppressed XAFS (a) Illustration of 1s2p ($K\alpha$) resonant inelastic X-ray scattering (b) Illustration showing the feasibility of “lifetime broadening-suppressed” XAFS measurement

Then, I noticed another point: even if the inelastic X-ray scattering spectrum is measured under conditions yielding a practical strength (i.e. nearer to resonance), it may be possible to determine the oscillator strength distribution $dg_{is}/d\omega$, as a highly true representation of the actually measured spectrum through numerical calculation using the Formula (1). In other words, it may be possible to determine “the lifetime broadening-suppressed XAFS” from the resonant inelastic scattering by repeating the procedures shown in the flow chart in Figure 2.

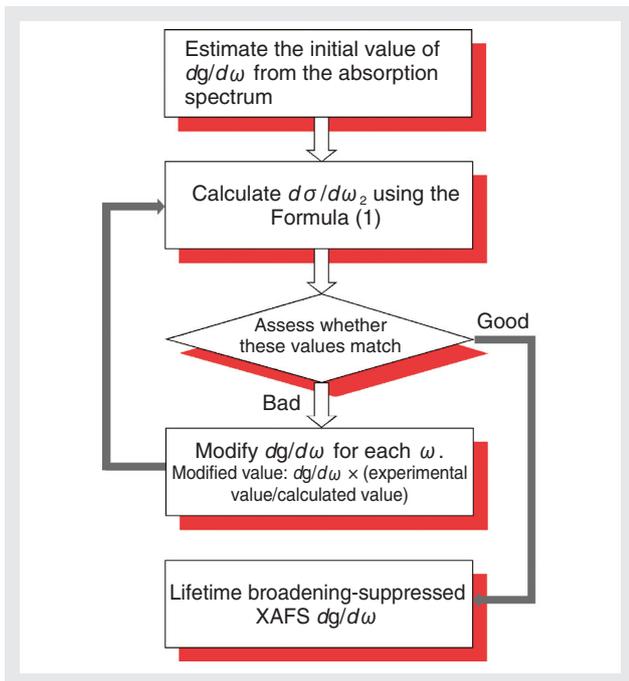


Figure 2 Procedures for deriving the lifetime broadening-suppressed XAFS

Figure 3 and Figure 4 show some results^[8] attained using this approach. In Figure 3, normal absorption spectra are shown with broken lines. The marks “■” and “▽” indicate $dg_{is}/d\omega$ obtained through procedures shown in Figure 2, from the emission spectra measured using several excitation energies (Figure 4). Then, looking at Figure 4, the resonant inelastic X-ray scattering (shown with a red line) in the Cu $K\alpha_1$ region has the same form as a normal Cu $K\alpha_1$ for high excitation energies (≥ 8987 eV), but it changes dramatically with a decrease in excitation energy. For researchers familiar with normal X-ray fluorescence analysis, it may be unbelievable fact to see a Cu $K\alpha_1$ having a double peak structure (8983.1 eV), a triple peak structure (8982.1 eV) or an asymmetric band structure for over ~ 10 eV (8977.1 eV).

Following the procedures in Figure 2 will derive roughly the same $dg_{is}/d\omega$ from these “unusual” spectra, as shown

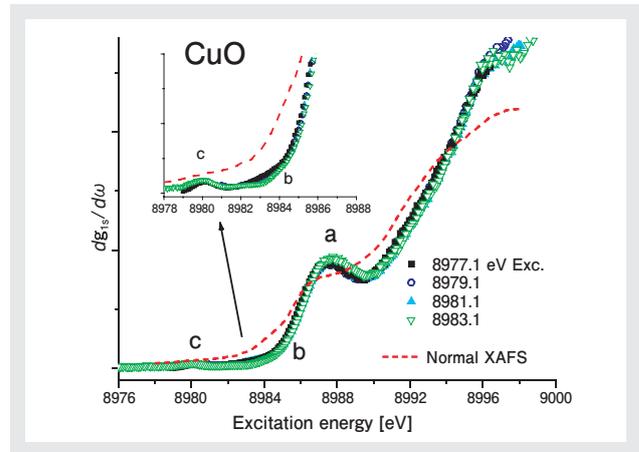


Figure 3 Normal XAFS spectrum of CuO (shown with a broken line), and lifetime broadening-suppressed spectrum (shown with symbols) derived from resonant inelastic scattering

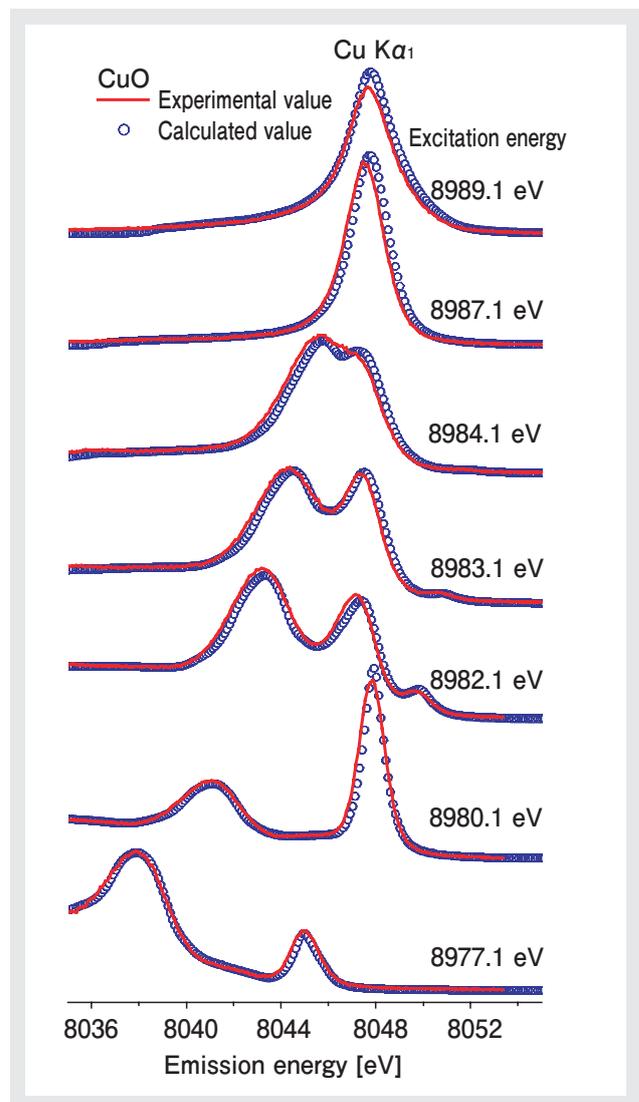


Figure 4 Resonant inelastic X-ray scattering spectra of CuO (shown with a red line) and inelastic scattering spectra (shown with marks “○”) calculated using the formula (1) with the spectrum of a 8983.1 eV excitation (shown with marks “▽”) in Figure 3

in Figure 3. In these “absorption spectra derived from resonant inelastic scattering spectra”, the section a (which, in a normal absorption spectrum, forms only a shoulder) becomes an independent peak. Also, the spectra clearly indicate the quadruple transition c (from 1s to 3d) and the bottom structure b, before a rise. It is evident that the absorption spectrum has a high resolution.

The spectra indicated using marks “○” in Figure 4 were determined using $dg_{1s}/d\omega$ (marked “▽” in Figure 3) derived analytically from the spectrum of 8983.1 eV excitation, and using Formula (1) for each excitation energy. It is evident that inelastic scattering spectra, which vary widely according to excitation energy, are reproduced truly using the same $dg_{1s}/d\omega$. The above results prove conclusively that the “unusual” behaviors of the X-ray fluorescence shown in Figure 4 result from emission governed by $dg_{1s}/d\omega$, and that the $dg_{1s}/d\omega$ represents “the lifetime broadening-suppressed” high-resolution XAFS through Kramers-Heisenberg formula.

Present Status and Future Prospect of Present Spectroscopy

Reference [2], published in 2002, is on the experimental application of the above-mentioned analysis method to CuO. A recent review of this document by Dr. Akio Kotani (in: “*J. Jpn. Soc. Synchrotron Rad. Res. (in Japanese)*” 18, 30 [2005]) contains the following passage: “[This method] can provide surprisingly detailed information on the fine structure, near the absorption edge, of CuL₂XAS (which is synonymous with XAFS – the author).” I, as the developer, believe that compared to the status in 2002, remarkable progress has been made until now regarding both accuracy of the experiment^[4] and the analysis method^[8-10].

The present spectroscopy can be applied to various tasks that cannot be easily tackled with conventional XAFS spectroscopy. The first application was in the study, mentioned above, of the fine structure of the vacant level of a copper compound, which is hidden under the bottom of the main transition^[2, 3, 8]. Later, the spectroscopy succeeded in observing the forbidden quadruple transition of a rare earth element by separating it from the dipole transition^[11]. Regarding Ho, in particular, even the fine structure of the transition from 2p to 4f was successfully observed^[12]. Moreover, regarding the observation of the spin selection XAFS for MnO, the spectroscopy succeeded in demonstrating that the previously reported spin selection XAFS method failed in making correct spin selection; and resolving the previously debated contradiction of related experimental results to Hund’s law^[5]. As for compounds of mixed valences, the spectroscopy showed that measurement of the valence

selection XAFS spectrum was feasible^[6, 7]. Regarding single crystals, more detailed information can be obtained by combining the spectroscopy with polarization experiments. This approach yielded interesting results from the spin selection polarization XAFS of LaMnO₃, which suggested that even in a paramagnetic phase, a spin order remained locally which had some characteristics of an antiferromagnetic phase^[13].

With the development of X-ray spectroscopy technology combined with synchrotron radiation, the present spectroscopy has found a rapidly expanding range of applications. Studies using the spectroscopy have already begun for high-temperature superconducting materials^[14] and bulk magnetic materials^[13]. Supported catalysts and complex solutions have also begun to be treated as objects of measurement. It will soon become possible to include such rarefied systems as samples from living organisms in the targets of the spectroscopy.

Conclusion

The present spectroscopy may seem acrobatic, as it uses “emission” to measure “absorption”, and thereby overcome difficulties proper to the absorption method. However, it appears that the spectroscopy has already departed the stage of basic development, and is entering the stage of application. My best hope is to see this spectroscopy serve many people as a tool to monitor various minute but important condition changes of a variety of functional materials.

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