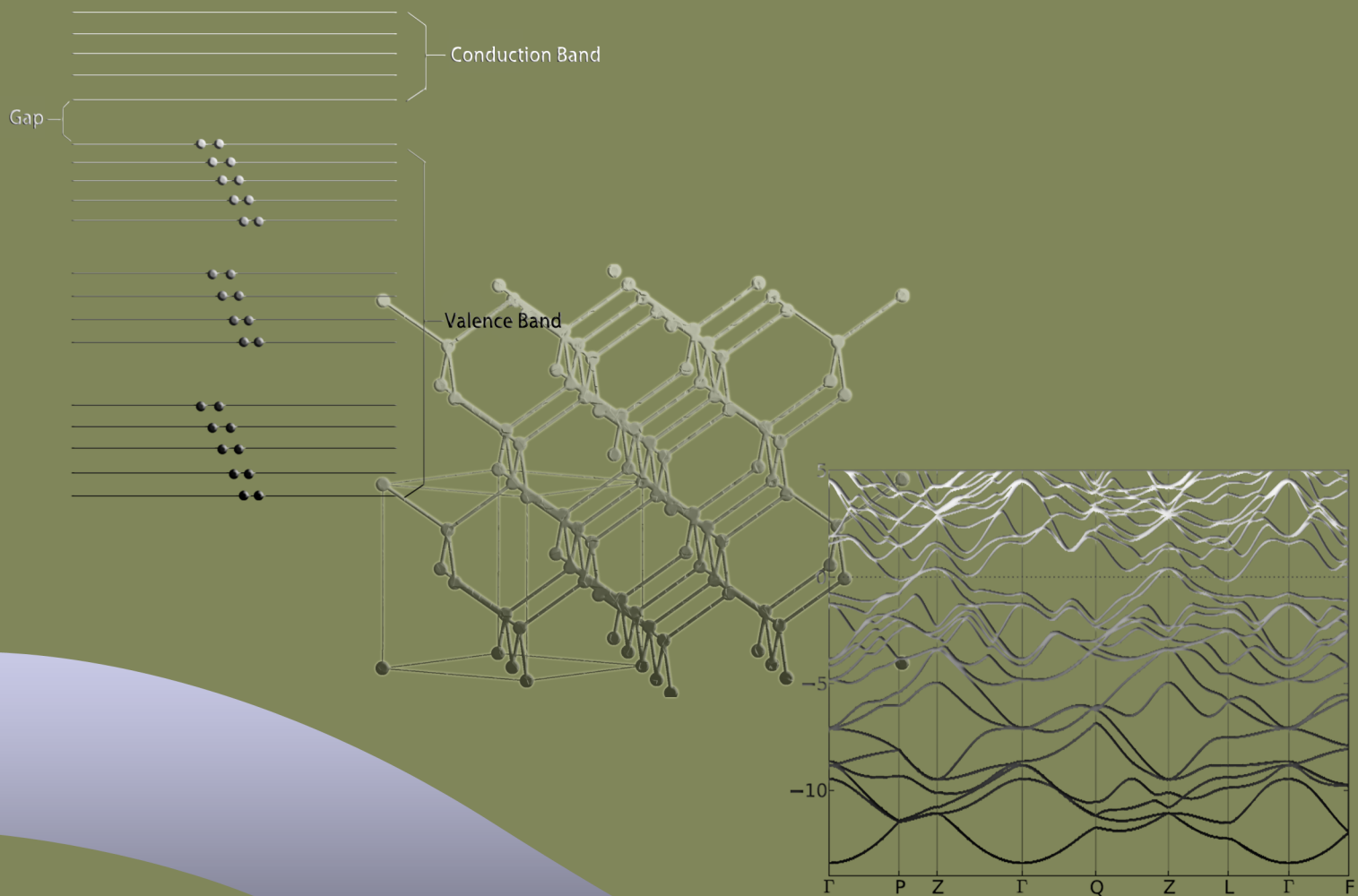


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XAFS Fluorescence Measurement



Introduction

For the measurement of XAFS signal, we have several choices including Transmission mode, Electron yield detection and Fluorescence mode. Among these techniques, the transmission mode was commonly used in our measurement due to the simple procedures and less requirement for sample. And also transmission mode could provide average information of the whole measured sample. Although with the development of measurement techniques, the requirement for sample is already not that strict as before, which makes transmission mode accessible for many samples, the other two techniques have its own advantages. For example, the electron yield measurement is more sensitive to the surface which favors the exploration into surface termination of specific materials. And in this script, we focus on the fluorescence mode to discuss its advantage and application.

1. Importance of Fluorescence Mode

When incoming X-ray was absorbed by material, photoelectron will be excited to corresponding accepted state. As the photoelectron propagates in the material, it will decay to the core level which is lower in energy level and hence more stable for electrons to stay. There are mainly two ways for photoelectrons to decay: one is through passing the energy to electrons in inner level such as L-level leading to the creation of so-called Auger electron, and the other one is direct jumping back (see Fig. 1) to specific inner level to emit light which is just the fluorescence used for X-ray absorption measurement. And the reason fluorescence can be used to measure X-ray absorption is easy to

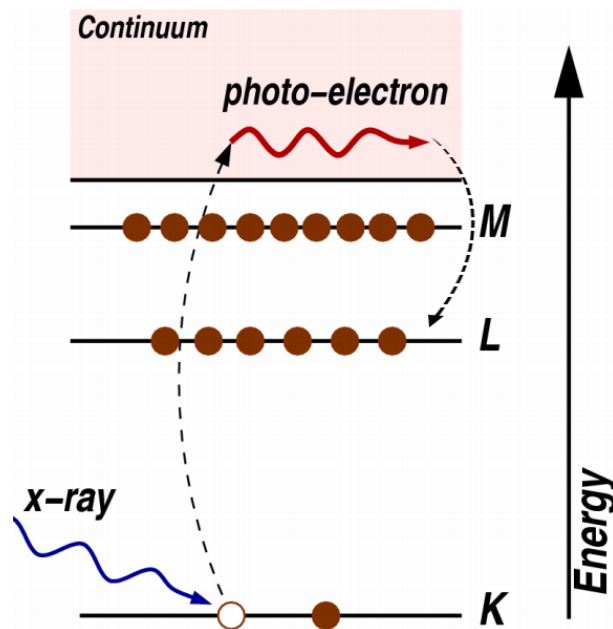


Figure. 1 Fluorescence mechanism.

understand, the more X-ray absorbed, the more fluorescence will be created and hence be detected.

Especially for XANES measurement when the absorption and fluorescence happens at the near-edge level, the detected fluorescence will also (the absorption is obviously tuned by near-edge level, so 'also' is used here) be seriously influenced by near-edge level (the final state for XANES absorption). This could provide more details for XANES spectrum.

In another way, we have the expression for absorption coefficient μ :

$$\mu = \frac{\rho Z^4}{AE^3} \quad (1-1)$$

where ρ is the density of material, Z is atomic number, A is atomic mass and E is X-ray energy. From expression - (1-1) we can see that the absorption coefficient is proportional to atomic number. Hence different element should possess distinguishable penetration depth ($pd = 1/\mu$), and this can be used for speciation application. The above two advantages are just where the other two measurement routes cannot help.

2. Absorption and Fluorescence

The incoming X-ray penetrates into depth x with specific probability which is tuned by element and many other properties. The X-ray can then be absorbed by atoms within dx area, and finally part of excited photoelectrons should decay back to core-level to emit fluorescence as discussed above. The whole process is illustrated in Fig. 2.

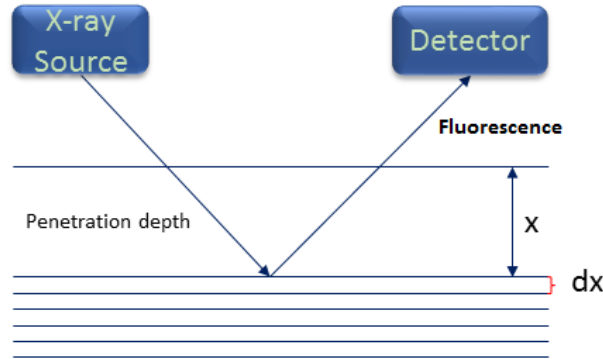


Figure. 2 X-ray absorption and corresponding fluorescence.

When fluorescence was created, it needs to travel back through the material to be detected by the detector as shown in Fig. 2. During the traveling, the fluorescence light can be scattered by surroundings, or can be absorbed again by surrounding atoms, etc. All of these factors contribute to the changing of fluorescence intensity detected, which leads to the fluorescence not directly (linearly) linked to the absorption. Considering all above factors, the relationship between absorption and fluorescence becomes[1]:

$$I_f = I_0 \frac{\epsilon \Delta \Omega}{4\pi} \frac{\mu_x(E) \{1 - e^{-[\mu_{tot}(E)/\sin\theta + \mu_{tot}(E_f)/\sin\phi]t}\}}{\mu_{tot}(E)/\sin\theta + \mu_{tot}(E_f)/\sin\phi} \quad (2-1)$$

where ϵ is the fluorescence efficiency, $\Delta\Omega$ is the solid angle of the detector, E_f is the energy of the fluorescence X-ray, θ is the incident angle (between incident X-ray and sample surface), ψ is the exit angle (between fluoresced X-ray and sample surface), $\mu_\chi(E)$ is the absorption from the element of interest, and $\mu_{tot}(E)$ is the *total absorption* in the sample, and we have:

$$\mu_{tot}(E) = \mu_\chi(E) + \mu_{others}(E) \quad (2-2)$$

In the limit of sample thin enough or thick dilute, the expression - (2-1) becomes the commonly used one:

$$I_f = I_0\mu \quad (2-3)$$

For details about the derivation of the expression for fluorescence, see Ref. [1], furthermore, next section will discuss what will happen when measured sample becomes thick or dense using fluorescence mode.

3. Self-absorption

As discussed in section 2, there is certain limitation for samples used for fluorescence XAFS measurement, which is the samples should be either thin or thick dilute. When sample becomes thick or dense, *self-absorption* process would dominate, which makes the measurement of XAFS signal using fluorescence mode not applicable.

As what it literally reveals, '*self-absorption*' refers to the process where the fluorescence is absorbed by material itself when traveling back through the material to the detector. Actually when two atoms are too close to each other, the fluorescence of one atom will be absorbed again by neighbouring atom, hence such process happens: *absorption* \rightarrow *fluorescence* \rightarrow *absorption* \rightarrow *fluorescence* \dots like a chain. The result is that little incoming X-ray intensity could trigger strong fluorescence. Moreover, the escape length is always longer than penetration depth, which means all fluorescence can be detected. So the detected fluorescence intensity in this case does not depend on real absorption thus useless for XAFS measurement.

References

- [1] Newville. Matthew. Fundamentals of xafs. pages 1–41, 2004.

