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Contribution of Multielectron Transitions to XAFS

Masao TAKAHASHI*, Shuichi EMURA*, Kazuhiko OMOTE**,
Shinzo YOSHIKADO†, Yoshiaki ITO††, Noritaka TAKAHASHI††,
and Takeshi MUKOYAMA††

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The energy dependence of amplitude reduction factor, s_0^2 for Kr is evaluated based on multielectron excitations from an X-ray absorption experiment. By convoluting the backscattering amplitude and adding the cross sections of multiple transitions to the theoretical values for single electron process reported by McMaster et al. [Lawrence Livermore Laboratory Report No. UCRL-50174, 1969], the contribution of the multiple processes to XAFS in solid Kr is investigated.

KEY WORDS: Multielectron Transitions/ X-ray Absorption/ Kr/ Backscattering Amplitude

1. INTRODUCTION

The works have been reported by many workers on multiple transition processes in the X-ray absorption in solids,[1–12] gases,[13–23] and vapor,[24] and give important suggestion on the interaction between atom and electron. It is generally considered that such processes do not contribute only to XANES, but also to XAFS far above the edge. For example, they have been identified in some cases (including K+M transitions).[10–12] On the other hand, there exists a number of earlier reports of multielectron absorption edges in solid targets on K+L,[1–5] L+L,[7,8] and K+K[9] transitions in XAFS.

Recently, it was pointed out by Kodre et al.[25–27] and Frahm et al.[28] and Ito et al.[29] that, since in solid the oscillations due to the XAFS would mask small signals (K+L transition edges) in the energy region where multiple electron excitation occurs. From the measurements of the Auger satellite intensities of Ar, Armen et al.[18] found that the shakeup probability has a sharp threshold onset and reaches to its asymptotic value at the energy close to the threshold, while the shakeoff probability increases gradually with photon energy. Crasemann,[13] Ito et al.,[23] and Schaphorst et al.[30] also indicated that the edges observed in X-ray absorption spectra are ascribed to the shakeup process only.

In the present study, we executed XAFS analysis of X-ray absorption in Kr using the backscattering amplitude of Kr in order to elucidate the contribution of the multielectron transitions to XAFS.

* 高橋昌男, 江村修一 : The ISIR, Osaka University, Mihogaoka Osaka 567, Japan.
** 表　和彦 : ERATO JRDC, Research Institute for Electric and Magnetic Materials, Sendai 980, Japan.
† 吉門進三 : Department of Electronics, Doshisha University, Kyoto 602, Japan.
†† 伊藤嘉昭, 高橋紀隆, 向山　毅 : ICR, Kyoto University, Kyoto 611, Japan.

2. EXPERIMENTAL

The absorption spectra for Kr were measured using the beam line BL-6B of the Photon Factory Ring in KEK, Tsukuba, with 2.5 GeV positrons at a circular current of 260–360 mA for 24 hr. The radiation was monochromatized with a Si(311) channel cut crystal and the calculated energy resolution (combined intrinsic crystal resolution and vertical angular divergence of the beam) was less than 3 eV at the KrK edge. The intensities of X-ray beam were measured with two ionization chambers filled with Ar gas before and after the sample chamber. Kr sample was contained at pressure of 1.19 atm in a sealed cell of 50 mm long having kapton windows. In order to lower the noise level of the detection system, the low-pass filter was used between the current to voltage and voltage to frequency conversion. The contribution of higher harmonics in the X-ray radiation is negligible due to the critical energy of the synchrotron radiation spectrum. We also confirmed the absence of spurious features (glitches or umweganregung reflections) due to the monochromator in $\ln(I/I_0)$, where I_0 is the intensity of incident photons and I is that of photons after passing through the Kr sample.

3. RESULTS AND DISCUSSION

Ito et al.[23] showed that the structures in the X-ray absorption spectra above the KrK edge can be explained as due to the shakeup process and indicated that the understanding of the transition process involved in multiple electron excitation is important to interpret the photoabsorption spectra. By comparing our data with the theoretical values for single electron process (including photoelectric,[31] coherent,[32] and incoherent[33] cross sections) reported by

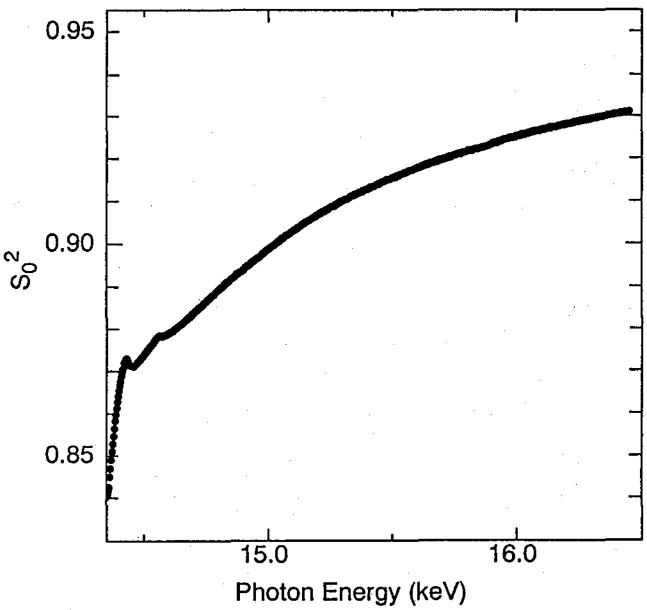

Fig. 1. The amplitude reduction factor, s_0^2 $(=1-p)$ as a function of energy past edge, due to multielectron process for Kr. p is the multielectron excitation probability.

McMaster et al.,[34] the amplitude reduction factor, s_0^2 is obtained due to the multielectron process (shakeup and shakeoff) (Fig. 1). s_0^2 is somewhere between 0.90 and 0.95 at high k. Since there is no oscillatory absorption structure like XAFS for monatomic gases such as Kr, a Zn foil (15 μm in thickness) was used in order to investigate the effect of the low-pass filter in the detection system. The results are shown in Fig. 2. As seen in Fig. 2, a very fine structure was observed in the filter method which resulted in a good signal to noise ratio. The fine structure may be attributed to the long distance neighbors. X-ray absorption spectra of Kr gas were measured using the filter method and, to elucidate the contribution of the multielectron processes, XAFS analysis[35] was executed on the photoabsorption spectra convoluted the backscattering amplitude of Kr together with the shakeup probability. The XAFS spectra of these model are presented in Fig. 3. The models (a), (b), (c), and (e) with the shakeup probability of K+M transitions could not obtain good fits to the simulated XAFS data in determining the background. It is considerable that the multielectron transition process may distort the XAFS. Therefore, for the XAFS studies, it is necessary to remove multielectron excitation.

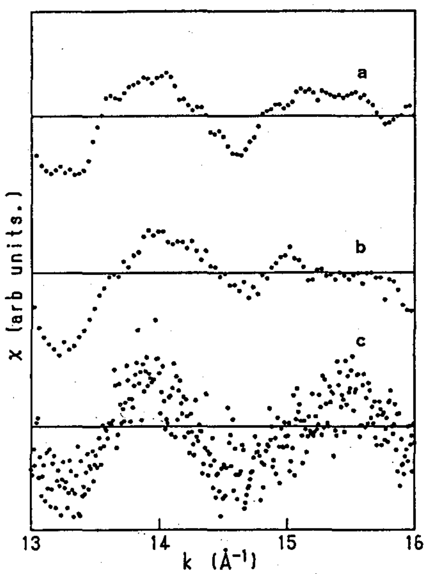

Fig. 2. XAFS of Zn foil with and without the low-pass filter.
(a) XAFS at a sampling time, 6 sec with the low-pass filter.
(b) XAFS at a sampling time, 3 sec without the low-pass filter.
(c) XAFS at a sampling time, 1 sec without the low-pass filter.

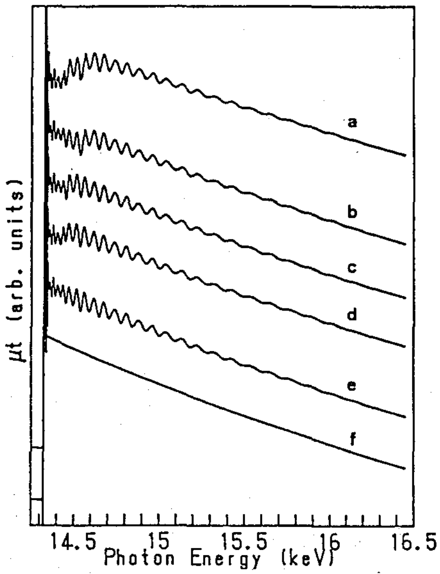

Fig. 3. The simulation of X-ray absorption spectra on Kr including multielectron transition process.
(a) (b)+1s3p shakeup transition probability, 0.83% of KrK edge jump.
(b) (f)+the backscattering amplitude. σ^2=0.008 Å^2, λ=5 Å.
(c) (e)+1s3p shakeup transition probability, 3% of KrK edge jump.
(d) (e)+1s3d shakeup transition probability, 4% of KrK edge jump.
(e) (f)+the backscattering amplitude of Kr. σ^2=0.01 Å, λ=5 Å.
(f) Theoretical values for single electron process reported by McMaster et al.[34]

4. CONCLUSION

The multielectron transitions of Kr, especially, K+M absorption edge distort the XAFS oscillations and we found some difficulty in determining the background. Our result is in agreement with that reported by Li et al..[12] It is indispensable to perform more systematic measurements on multielectron transitions in photoabsorption for various systems in order to elucidate the contribution of the multiple processes to the XAFS. Further investigations for other elements are being in progress.

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