JAPANESE JOURNAL OF APPLIED PHYSICS
VOL. 28, NO. 3, MARCH, 1989, pp. L 513–L 514

Photoacoustic EXAFS of Solid Phase

Tsutomu MASUJIMA, Hideaki SHIWAKU, Hisanobu YOSHIDA,
Mikio KATAOKA†, Michael REICHLING††, Hideo IMAI†††,
Hiroshi KAWATA††††, Atsuo IIDA††††, Atsushi KOYAMA††††
and Masami ANDO††††

Institute of Pharmaceutical Sciences, Hiroshima University, School of Medicine, Hiroshima 734
†Faculty of Sciences, Tohoku University, Sendai 980
††Fachbereich Physik, Freie Universitat Berlin, WE 1, Arnimallee 14, 1000 Berlin 33, West Germany
†††Faculty of Pharmaceutical Sciences, Fukuyama University, Fukuyama 729-02
††††National Laboratory for High Energy Physics(KEK), Tsukuba 305

(Received January 17, 1989: accepted for publication February 13, 1989)

Fine structures observed in X-ray photoacoustic spectra of various solids were compared with those in the absorption spectra. For a precise comparison, the photoacoustic spectra were corrected for energy-depending X-ray absorption of gas existing in the optical path. Finally corrected photoacoustic spectra showed a leveled or decreasing trend with increasing photon energy. Good correspondence between the X-ray photoacoustic spectra and the absorption spectra further confirmed that the fine structures in the photoacoustic spectra are identical with the extended X-ray absorption fine structures (EXAFS).

KEYWORDS: photoacoustic spectroscopy, EXAFS, synchrotron radiation, X-ray absorption

§1. Introduction

X-ray absorption spectroscopy is now widely used in the characterization of materials. In these fields, the extended X-ray absorption fine structure (EXAFS)[1] methods based on the various effects of X-ray absorption are now widely employed as powerful tools for atomic structure analysis. As a further effect of X-ray absorption, heat generation should also be considered. Recently, the heat generation by monochromatic X-ray irradiation was detected by means of a microphonic photoacoustic (PA) method using the synchrotron radiation,[2] and further spectroscopic study showed a fine structure in its primitive spectrum.[3] In the meanwhile, a theoretical study was also started to explain the phenomena using our primitive spectrum.[4] In these circumstances, further studies using various samples were performed in order to check the truth and generality of this phenomenon and to study the common features.

§2. Experimental

The monochromatic X-ray was obtained by Silicon (111) double crystals at Beam Line 4A of the Photon Factory, Japan. The X-ray photoacoustic (PA) cell and the instrumentation have heen detailed elsewhere.[2,5] Ionization chambers were set on both sides of the PA cell in order to compare the PA spectrum with the simultaneously detected absorption spectrum.[5] A chopper rotating at the chopping frequency, 10 Hz, was set at the upstream of these detectors. The solid samples were Cu and Ni foils with various thicknesses, $NiSO_4$, $NiCl_2$, and $CuSO_4$. The metal foils were rolled thin films and were all purchased. Other chemicals were all of reagent grade and used as received.

§3. Results and Discussion

Figure 1 shows a primitive PA spectrum (a) and an absorption spectrum (d) of a Ni foil sample (5 μm thick). The corresponding fine structure seems to show that the EXAFS is also reflected in the PA spectrum, in other words, in the heat generation. The only difference between these two spectra is a trend for the PA signal to increase monotonously with increasing photon energy. However, this primitive spectrum which was normalized to the first ionization chamber current should be corrected for the energy-dependent X-ray absorption by gas (air) existing in the optical path. The effective X-ray flux

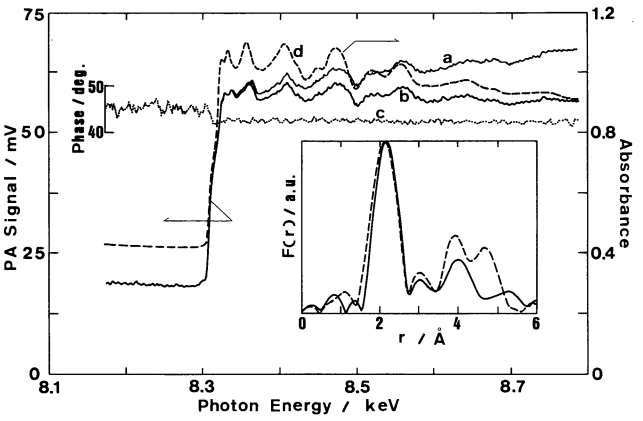

Fig. 1. X-ray photoacoustic spectra of the primitive data of signal amplitude (a), the corrected signal amplitude using eq. (1) (b) and phase (c), and the absorption spectrum (d) of a nickel foll (5 μm). Chopping freq. 10 Hz. The inserted figure is the results of a Fourier transform of Kai components of the X-ray photoacoustic (solid line) and the absorption spectra (broken line).

at the surface of the sample, I, can be estimated by the following equation.

$$I = k \times IC_0/(1-\exp(-\mu(E)\rho x_1) \times \exp(-\mu(E)\rho x), \quad (1)$$

where IC_0 is the upstream ion chamber current; $\mu(E)$ is a mass absorption coefficient at a photon energy, E; ρ is a density of air; x_1 is the length of the ionization chamber; and x is the total optical length from the inlet face of the ionization chamber to the surface of the sample. The first term of eq. (1) is a correlation constant, k; the second is the correction for ionization yield due to the energy dependence of the absorption coefficients; and the third is the correction for the gas absorption throughout the optical path. By this correction, the primitive spectrum ((a) in Fig. 1) was changed to show a slight decreasing trend (as (b)), like the absorption spectrum as shown in Fig. 1.

The atomic radial dispersions were obtained by the Fourier transform analysis[6,7] of the fine structures of the PA and the absorption spectra as shown in the insertion of Fig. 1. These dispersions are similar to each other, especially in the peak positions of the nearest neighbor atomic distances, and this further confirms that the photoacoustically detected fine structure is the EXAFS.

The phase spectrum shows the average depth of the heat generation which originates from an exponential X-ray absorption profile in the material. This phase value was the output from the lock-in amplifier with offset of +180 degrees, i.e., $-\theta+180$ degrees. It is interesting that the phase value decreases, i.e., θ increases, stepwise at the K-edge point. This means the average depth of the heat generation became deeper from the surface due to an increase in absorption coefficient.

The aforementioned solid samples were all tested in the same procedures. As an example, Fig. 2 shows the EXAFS spectra of $NiSO_4$ and the result of its Fourier transform. Since the PA detector is not sensitive enough at present, the PA EXAFS of a sample at lower metal content is a little noisy, and these noises also seems to be converted by the Fourier transform to higher $F(r)$ values seen in the radial dispersion above 4.5 Å. The phase spectrum is almost constant on account of the signal from the surface of the inorganic powder, which has a small heat diffusion coefficient and a high surface area. Commonly observed good correspondence in the fine structures and the similarity of the radial dispersions between the results obtained by the photoacoustic and absorption methods confirmed our first conclusion that the fine structures in the X-ray photoacoustic spectra are the EXAFS.[3] The interpretation of these phenomena from theoretical and experimental viewpoints is now in progress. Garcia *et al.* have applied their theory to our primitive data with an abnormally high ratio of the fractions of energy-heat conversion.[4] This finally corrected data should be useful for further theoretical investigations. The photoacoustic method can be applied to all types of shapes and states of the sample and also to non-destructive depth profiling, and this finding will greatly expand the methodology of EXAFS.

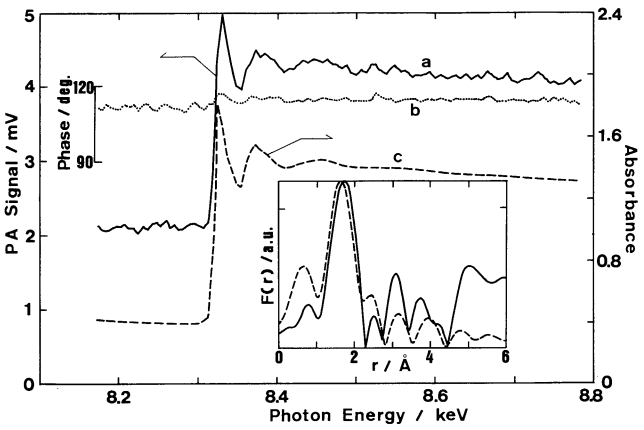

Fig. 2. The X-ray photoacoustic spectra of the corrected signal amplitude (a), phase (b), and the absorption spectrum (c) of a $NiSO_4$ powder. Chopping freq. 10 Hz. The inserted figure is the results of a Fourier transform of Kai components of the X-ray photoacoustic (solid line) and the absorption spectra (broken line).

Acknowledgment

This work was performed as a cooperative research project (Nos. 86-020 and 88-089) at the Photon Factory, KEK, Japan. Financial support in the form of a Grant-in-Aid for Scientific Research (No. 62570968) from the Ministry of Education, Science & Culture Japan is greatly appreciated.

References

1) B. K. Teo: *EXAFS: Basic Principles and Data Analysis* (Springer-Verlag, Berlin, 1986).
2) T. Masujima, H. Kawata, Y. Amemiya, N. Kamiya, T. Katsura, T. Iwamoto, H. Yoshida, H. Imai and M. Ando: Chem. Lett. **1987** (1987) 973.
3) T. Masujima, H. Kawata, M. Kataoka, M. Nomura, K. Kobayashi, M. Hoshi, C. Nagoshi, S. Uehara, T. Sano, H. Yoshida, S. Sakura, H. Imai and M. Ando: Photon Factory Activity Report **5** (1987) 139.
4) M. E. Garcia, G. M. Pastor and K. H. Bennemann: Phys. Rev. Lett. **61** (1988) 121.
5) T. Masujima, H. Kawata, M. Kataoka, H. Shiwaku, H. Yoshida, H. Imai, T. Toyoda, T. Sano, M. Nomura, A. Iida, K. Kobayashi and M. Ando: to be published in Rev. Sci. Instrum.
6) D. E. Sayers, E. A. Stern and F. W. Lytle: Phys. Rev. Lett. **27** (1971) 1204.
7) M. Nomura: *Documentation on the Operation of BL7C at Photon Factory* (National Laboratory for High Energy Physics, Tsukuba, 1987) KEK Internal 87-1.