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Novel approach for structure analysis by x-ray Raman scattering

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An oscillation similar to that in extended x-ray absorption fine-structure (EXAFS) measurements was observed in the x-ray Raman spectra of graphite by exciting 8265-eV x rays from synchrotron radiation. From an analysis employing the formula used for EXAFS, the carbon-carbon interatomic distances are obtained which are in good agreement with the known values in graphite. Thus, x-ray Raman scattering by hard x rays is a very promising method for the determination of the local structure around light elements.

For noncrystalline materials extended x-ray-absorption fine structure (EXAFS) is now an established tool for the determination of local structures around a central atom.[1-3] An application of EXAFS to the elements with low atomic number is, however, limited to thin films or surfaces because K absorption edges lie in the soft x-ray region where the experiment is not feasible in air and adequate window materials are not available.

Inelastic x-ray scattering using hard x rays may supply the same information as the absorption. It corresponds to using optical Raman scattering instead of infrared absorption. The phenomenon of x-ray Raman effect has been pointed out as early as the 1920s. It was, however, only 1967 when the relationship between x-ray Raman scattering and x-ray absorption was revealed by Mizuno and Ohmura.[4] Their theory predicts a transition probability proportional to[5]

$$(1+\cos^2\theta)\sin^2(\theta/2)\left|\int \Psi_1^*(r)r\Psi_0(r)dr\right|^2 , \qquad (1)$$

where θ is the scattering angle and Ψ_0 and Ψ_1 are the initial- and final-state wave function. Therefore, the spectrum of x-ray Raman scattering should essentially be the mirror image of the K-absorption spectrum except for the angle dependence of the intensity. This was immediately confirmed experimentally for beryllium by Suzuki.[6] Since then x-ray Raman scattering has been investigated by many workers,[5-12] but the detailed features have never been observed; the extreme weakness of the scattering intensity did not allow a spectrum with sufficient resolution and single-to-noise ratio.

Recently, synchrotron radiation (SR) has made it possible to supply an x-ray flux several orders of magnitude more intense than the characteristic lines available from a rotating anode x-ray generator. Therefore, by using SR it should be possible to improve both the intensity and the resolution. In this report the x-ray Raman spectrum of graphite has been studied with SR to see whether or not the spectrum has an EXAFS-like oscillation from which structural parameters can be extracted.

The experiment was carried out at beam line BL-10C of the Phonton Factory at the National Laboratory for High

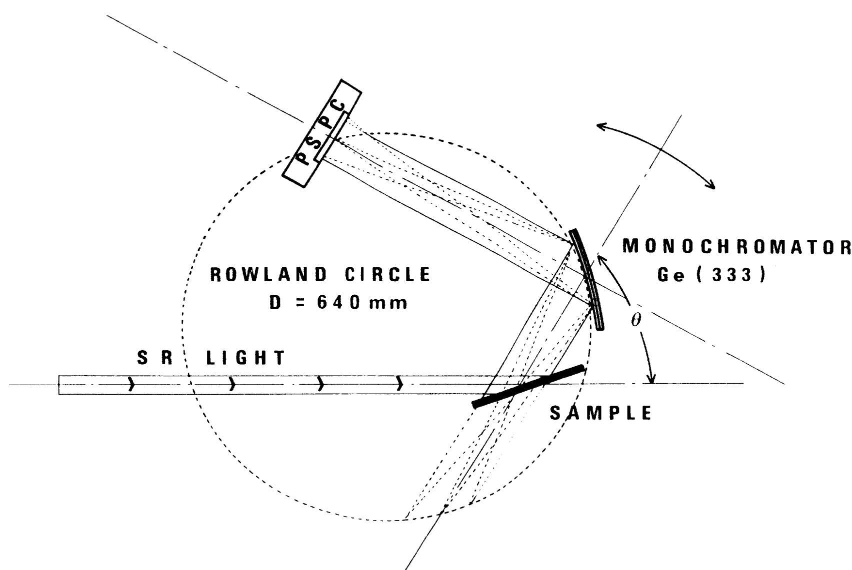

FIG. 1. A schematic diagram of the experimental setup for x-ray Raman measurement. PSPC is the position sensitive proportional counter.

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Energy Physics (KEK)[13] with the ring current between 100 and 250 mA at 2.5 GeV. The optics of this beam line consist of a double Si(111) crystal monochrometer and a double-focusing mirror coated with platinum. The intensity of x rays was estimated to be 10^{10} photons/sec at 8 keV with a resolution better than 2 eV. This intensity is about 50 times as much as that of Cu $K\alpha_1$ line from a 12 kW x-ray generator focused with a LiF(220) curved crystal. The scattered x rays were measured by using the apparatus shown in Fig. 1, which is similar to the one proposed by Pattison *et al.*[11] A curved Johansson-type Ge(333) crystal with Rowland radius of 320 mm (Ref. 14) is positioned about 100 mm from the sample. The sample is placed in a defocused position relative to the analyzer crystal. The scattered radiation from the sample is brought to a focus at a distance of 485 mm from the analyzer crystal. At this position a position-sensitive proportional counter (PSPC) was placed at a focal plane and serves to detect as well as to locate scattered photons. The analyzer crystal and the PSPC can be rotated around the sample so as to be able to obtain an angle dependence of the scattering. The data were always accumulated until counting statistics better than 1% were achieved.

Figure 2 shows a typical example of the x-ray scattering spectrum collected at a scattering angle of 60°. This angle was chosen because the scattering intensity is strong [see Eq. (1)] while overlap with Compton scattering is not so serious. A sharp peak at the energy of 8265 eV is the Rayleigh scattering, whose width [6 eV at full width at half maximum (FWHM)] represents the energy resolution of this experimental condition. A broad peak shifted by 70 eV from Rayleigh scattering is the well known Compton scattering. X-ray Raman scattering is observed beyond 284 eV. The energy coincides with the binding energy of K electrons in the carbon atom, and agrees very well with previously reported values.[5,6] The contribution from Compton scattering was fitted to a Lorentz function and subtracted. The resultant x-ray Raman spectrum is shown in Fig. 3 in expanded scale and an extended oscillation is clearly observed. This oscillation was reproducible in repeated experiments and in spectra with a scattering angle of 90°.

Since Eq. (1) has the same integral with the expression for absorption, the following equations used for EXAFS analysis should also be applicable in order to obtain the radial structure function $\Phi(r)$ from the observed oscillation $\chi(k)$,

$$\chi(k)=\sum_j (N_j/kr_j^2)F_j(\pi,k)\times\exp(-2k^2\sigma_j^2-2r_j/\lambda)\sin[2kr_j+\alpha_j(k)]\ , \quad (2)$$

$$\Phi(r)=\int k^2\chi(k)\exp(-ikr)dk\ , \quad (3)$$

where N_j is the number of atoms in the jth shell, $F_j(k)$ is the scattering amplitude which is a function of photoelectron's wave vector k, σ_j is the Debye-Waller factor, and α_j is the phase shift. R_j is the distance from the central absorbing atom to the atoms in the jth shell. λ is the mean free path of the photoelectron in the solid. In the following, an attempt to extract structural parameters using the above equations will be described.

A smooth background was estimated by using a second-order least-squares fit over a fixed interval around each data point and subtracted. The resultant oscillatory part was converted to k space and multiplied by k^2 to partially compensate the decay of the EXAFS amplitude function. The detailed procedure has been described elsewhere.[15] Figure 4(a) shows the oscillation extracted from the spectrum of Fig. 3. The associated Fourier transform of the oscillation, the radial structure function, is shown in Fig. 4(b), where the transform was taken over the wave number range of $1.6 < k < 9.0$ Å^{-1}. The phase factor was included in the calculation by using theoretical phase shifts for carbon.[16] Two peaks are clearly observed at distances of 1.43 and 2.48 Å in Fig. 4(b). There are three carbon-carbon distances in graphite; 1.42, 2.46, and 2.84

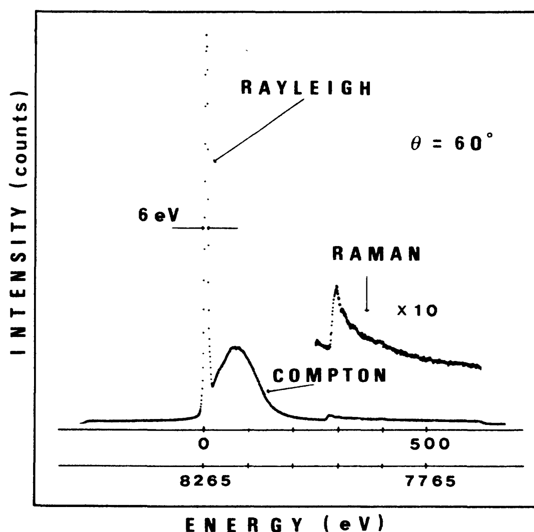

FIG. 2. Inelastic x-ray scattering from graphite observed at 60 degrees. The abscissa is expressed both by the energy and the energy shift.

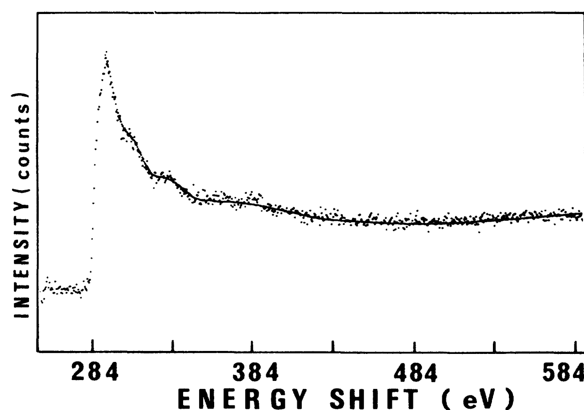

FIG. 3. X-ray Raman spectrum derived by subtracting the contribution from Compton scattering. Dots, observed; solid line, smoothed.

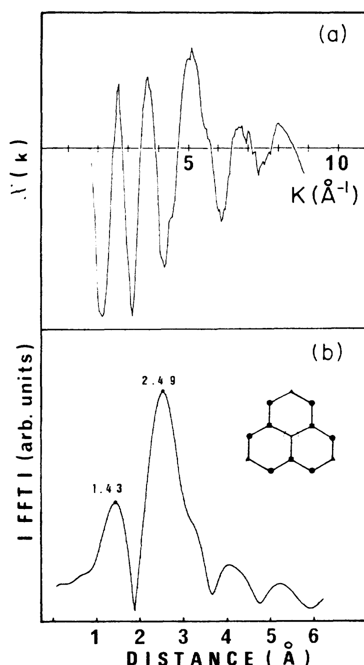

FIG. 4. (a) Extended oscillation and (b) associated Fourier transform (radial structure function) of graphite.

Å. Therefore, the observed two peaks in the radial structure function exactly correspond to the first two neighbors and the third one may correspond to a shoulder of the second peak. The radial structure function of graphite obtained from the analysis of electron energy-loss spectra (EELS) has been reported by Kincaid *et al.* [17] and the two measurements are in close agreement with each other. Following the routine of EXAFS analysis, curve fitting was also tried for the first shell and the results are listed in Table I. Curve fitting was not attempted on the other shells because the second and the third peaks are not resolved in the Fourier transform.

We can conclude that the extended oscillations in x-ray

TABLE I. Structural parameters obtained by curve fitting for the first peak of the Fourier transform shown in Fig. 4. The numbers in parentheses are those fixed in the least-squares calculations. N is the number of atoms, λ the mean free path, R the distance from the central absorbing atom to the atoms in the specified shell, θ is the Debye-Waller factor, and E_0 is the threshold energy.

Bond	N	λ (Å)	R (Å)	σ (Å)	E_0 (eV)[a]
C–C	(3)	1.2	1.44 ± 0.03	(0.06)	300

[a]Best-fit value of E_0 is 15 eV higher than observed threshold 285 eV. Similar discrepancy has been observed for the analysis of EXAFS data of low Z molecules (Ref. 18).

Raman scattering have the same information as EXAFS and that it is possible to extract structural parameters from the analysis of the oscillations. This technique is especially useful to determine local structures around an element with low atomic number for which absorption measurements are difficult. In this experiment the signal-to-noise ratio of 100 was achieved with a resolution of 6 eV at 8 keV. In the near future the signal-to-noise ratio was well as resolution of x-ray Raman spectroscopy should be improved by the use of high-brightness sources such as multipole wigglers. Under higher-resolution x-ray Raman spectra will also offer information on electronic states as x-ray-absorption near-edge structure (XANES) does.

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