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X-ray Raman scattering as a substitute for soft-x-ray extended x-ray-absorption fine structure

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We have recorded x-ray Raman-scattering spectra from graphite and diamond with high resolution and good signal-to-noise (S/N) ratio by excitation with hard x rays from synchrotron radiation. The scattering spectra show characteristics predicted by the theory. The observed scattering spectrum for graphite was not exactly the same as the absorption spectrum, possibly because of polarization effects in the anisotropic materials. In the case of diamond powder, however, oscillations identical with those found in the extended x-ray-absorption fine structure (EXAFS) spectrum were observed, and from an analysis employing the formula used for EXAFS, interatomic distances were obtained. Thus, it is experimentally confirmed for the first time that x-ray Raman spectroscopy by using hard x rays can supply the same information as the soft-x-ray EXAFS. X-ray Raman spectroscopy can thus be a substitute for EXAFS to determine the local structure around low-atomic-number elements whose EXAFS study is plagued with inherent experimental difficulties.

I. INTRODUCTION

Extended x-ray-absorption fine structure (EXAFS) is now an established tool for the determination of local structure around a selected central atom¹⁻³ in noncrystalline materials. The application of EXAFS to elements with low atomic number is, however, limited, in spite of the importance of carbon, nitrogen, and oxygen in materials science. Because their characteristic absorptions lie in the soft-x-ray region, where experiments are not possible under atmospheric conditions, and because adequate window materials are not available, everything from the x-ray source, monochromator to the detector, must be placed in vacuum. This is feasible in view of modern technology, but it is certainly not an easy task; in addition, the materials used are usually restricted to thin films or solid surfaces which can withstand a vacuum.

A way to evade this difficulty might be found in inelastic scattering instead of absorption, the relationship of the two being schematically shown in Fig. 1. Indeed, optical Raman scattering has been extensively used for a long time for materials to which infrared-absorption spectroscopy is hard to apply; for example, aqueous solu-

tions. The phenomenon of the x-ray Raman effect had been pointed out as early as the 1920s. It was, however, only 1967 when the first unambiguous x-ray Raman spectra were obtained for elements from beryllium to carbon by Suzuki⁴ and the relationship between x-ray Raman scattering and x-ray absorption was theoretically interpreted by Mizuno and Ohmura.⁵ Since then, x-ray Raman scattering has been intermittently studied by several authors,⁶⁻¹⁵ but the detailed features have never been revealed; the extreme weakness of the scattering prevented previous workers from obtaining a spectrum with sufficient resolution and, at the same time, with good enough signal-to-noise ratio.

In recent years synchrotron radiation has made it possible to supply an x-ray flux several orders of magnitude more intense than the characteristic lines available from a conventional rotating-anode x-ray generator, thus making it promising to obtain weak scattering spectra with good S/N ratios at higher resolution. Therefore, an effort to observe fine structures in the x-ray Raman scattering was made and the results on graphite were reported in a brief communication.¹⁶ This article is an extension of the previous effort; x-ray Raman spectra of improved quality were obtained for graphite as well as for its allotrope, diamond. Fine structures are inherent to each substance and, especially in the case of diamond, major features show a one-to-one correspondence with those found in the absorption spectrum. As a result, it is confirmed beyond a doubt that x-ray Raman scattering can be a substitute for soft-x-ray absorption and that it can be a very useful new method for structural studies around low-atomic-number elements.

II. EXPERIMENT

The experiment using synchrotron radiation was carried out at beam line BL-10C of the Photon Factory at the National Laboratory for High Energy Physics (KEK), Ibaraki, Japan, with ring current between 150

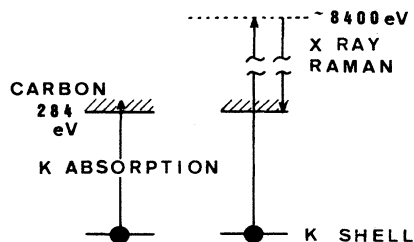


FIG. 1. Comparison of soft-x-ray-absorption spectroscopy and inelastic-scattering spectroscopy and inelastic-scattering spectroscopy using hard x rays.

and 250 mA. The optics of the beam line as well as the polychromator used in this experiment are the same as those described in the previous communication.¹⁶ The only difference is that a Ge(440) dispersing crystal was also employed in addition to Ge(333), in order to always ensure reproducibility of the result under different experimental conditions. For the excitation, x rays of 8900 and 8400 eV were chosen for Ge(440) and Ge(333) crystals, respectively, because these energies are close to that of the Cu $K\alpha$ line, and also because of geometrical requirements of the experimental set up. Scattered photons were accumulated by a position-sensitive proportional counter (PSPC) combined with a multichannel analyzer (MCA) for at least 24 h, and sometimes 3 d.

The number of photons of the exciting x rays was estimated to be $\sim 10^{11}$ cps from the output of an ionization chamber, which was calibrated by a solid-state detector whose quantum yield was assumed to be unity. The linewidth of the exciting x rays is estimated to be about 2 eV, and the resolution of the detection system is 6 eV, as was measured by the full width at half maximum (FWHM) of the Rayleigh scattering. The dispersion on the MCA was 1.39 eV/channel.

Preliminary experiments were carried out in the laboratory by the use of a rotating-anode x-ray generator (Rigaku RU-200) as an excitation source. Although the resolution is rather poor and detailed structure cannot be observed, as a whole this source gives spectra similar to those obtained from synchrotron radiation.

The diamond powder (particle size $< 1 \mu\text{m}$) was obtained from Tokai Diamond Co. and was kept between two Mylar films during the measurement. Pyrolytic graphite was kindly supplied by Professor Enoki of the Tokyo Institute of Technology and mounted such that the E vector of the x rays was parallel to the cleavage plane.

III. THEORY

Although the theory of x-ray Raman scattering was developed some 20 years ago,⁵ it is worthwhile to summarize it here very briefly as it will be convenient for the discussion later.

The nonrelativistic Hamiltonian which describes the interaction between electron and radiation is expressed by¹⁷

$$\begin{aligned} H_{\text{int}} &= H_1 + H_2 \\ &= -\frac{e}{m} p A + \frac{e^2}{2m} A^2. \end{aligned} \quad (1)$$

Here, H_1 and H_2 are interaction terms which are linear and quadratic in the vector potential A , and p is the electron-momentum operator. The transition probability w for photon scattering is expressed by

$$\begin{aligned} w &= (2\pi/\hbar) |\langle f, j | [H_1(2) + H_2(1)] | 0, i \rangle|^2 \\ &\quad \times \delta(E_f - E_0 - h(\nu_i - \nu_j)), \end{aligned} \quad (2)$$

where $|0, i\rangle$ and $|f, j\rangle$ mean initial and final states where the electronic state is 0 and the photon is in the state i , or

the electronic state is f and the photon is in j , respectively. E and ν represent the energy of the electron and the frequency of the photon indicated by the suffix. $H_1(2)$ and $H_2(1)$ indicate the second-order perturbation contribution from H_1 and the first-order contribution from H_2 , respectively. The well-known Kramers-Heisenberg equation for optical Raman scattering can be derived from $H_1(2)$ by assuming that the contribution from $H_2(1)$ is negligible. This assumption is valid in the optical region because photon wavelengths are much larger than the sizes of atoms.

The wavelengths of x rays are, however, close to the size of atoms and so the assumption above does not always hold. Still, the mean diameter of K -electron wave functions of heavy atoms is much smaller than the wavelength of x rays and the contribution from $H_1(2)$ can be dominant in such a case. This holds for the scattering of x rays of about 8 keV by copper studied previously, and the spectral change as resonance was approached was satisfactorily reproduced by a calculation based on the Kramers-Heisenberg equation.¹⁸

In the case of the scattering by K electrons of light elements like carbon, the electron mean diameter is about the same as that of x rays and the photon energy is almost 2 orders of magnitude larger than the ionization energy. As a result, the matrix elements of $H_1(2)$ diminish and do not contribute to the scattering.¹⁷ Therefore, only the term including $H_2(1)$ should be taken into consideration and after averaging over two possible directions of the polarization vector, we obtain

$$\begin{aligned} w &= \frac{4\pi^3 e^4 \hbar}{m^2 \nu_i \nu_j} (1 + \cos^2 \theta) |\langle f | \exp[i(k_j - k_i)r] | 0 \rangle|^2 \\ &\quad \times \delta(E_f - E_0 - h(\nu_i - \nu_j)), \end{aligned} \quad (3)$$

where θ is the scattering angle. If the scattering vector s is defined by $s = k_j - k_i$, it can be approximated by using the x-ray wavelength λ as follows,

$$s = 2k \sin(\theta/2) = (4\pi/\lambda) \sin(\theta/2), \quad (4)$$

because $k_i \sim k_j$. In the present case, $sr < 1$ in the region where the wave function $|0\rangle$ has significant value, so it is a good approximation to retain only the first two terms of the power-series expansion of the exponential in (3). Then the contribution of the first term of the expansion vanishes because of the orthogonality of the wave functions $|f\rangle$ and $|0\rangle$, and the substitution of the second term reduces to

$$w = \frac{64\pi^5 e^4 \hbar}{m^2 c^2} (1 + \cos^2 \theta) \sin^2(\theta/2) |\langle i | r | f \rangle|^2. \quad (5)$$

The matrix element of Eq. (5) is exactly the same as that for absorption. Thus, any theory that describes the EXAFS phenomenon can be applied to evaluate the intensity of the scattering, and the theory will eventually lead to the same formula, except for the angle dependence. According to single-scattering theory,¹⁻³ the EXAFS oscillation $\chi(k)$ may be expressed by a superposition of various sinusoidal waves as

$$\chi(k) = \sum_i \frac{N_i}{kR_i^2} F_i(k) \exp(-2\sigma^2 k^2 - 2R_i/\lambda) \times \sin(2kR_i + \phi_i), \quad (6)$$

and its Fourier transform gives a radial structure function $\Phi(R)$ whose peak positions and heights indicate interatomic distances and coordination numbers. Here, k is the photoelectron momentum, N_i and R_i are the coordination number and interatomic distance to the neighboring atom i , F_i is the backscattering amplitude, σ_i and λ are the Debye-Waller factor and the electron mean free path, and ϕ_i is the phase factor. Thus, after a procedure similar to that employed for EXAFS analysis, the same structural parameters can be obtained from the EXAFS-like oscillations which should appear in the x-ray Raman-scattering spectrum.

IV. RESULTS

Figure 2 shows typical scattering spectra from graphite and diamond observed at 60° or 90°. To the lower-energy

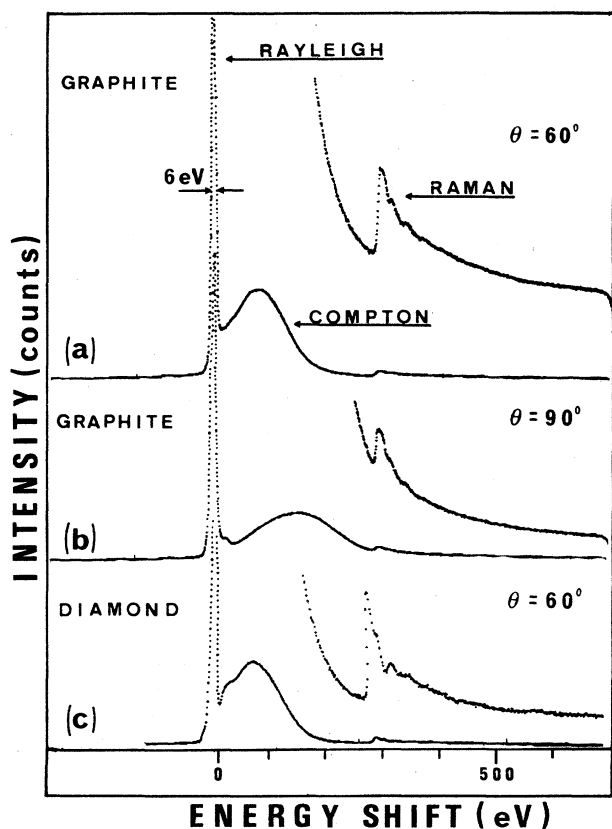


FIG. 2. (a) Inelastic-scattering spectrum from graphite observed at 60°. (b) Inelastic-scattering spectrum from graphite observed at 90°. (c) Inelastic-scattering spectrum from diamond observed at 60°. The Raman parts are inserted with an expanded scale. (a) and (b) were obtained with a Ge(440) dispersing crystal at 8900 eV excitation and (c) was obtained with a Ge(333) crystal at 8400 eV excitation. The Compton shift at 60° scattering does not coincide exactly for graphite and diamond because the excitation energy is slightly different.

side of the exciting light there is a strong, symmetric Compton scattering whose peak energy shifts with the scattering angle. The peak energies coincide with those calculated from the well-known equation, $\delta\lambda = (0.024 \text{ \AA}) (1 - \cos\theta)$. The Compton shift is slightly different in (a) and (c) because the excitation energy is somewhat different. A very weak signal which we assign as Raman scattering can be observed to the lower-energy side of the Compton scattering in each spectrum. After accumulating the signal for 3 d, the total count number at the Compton peak is typically 3×10^5 , and that at the Raman peak is 3×10^4 .

As can be seen in Figs. 2(a)–2(c), each Raman scattering has an EXAFS-like appearance: a steep edge as well as strong and sharp features near the edge, followed by a complicated oscillation. The energy shift of the edges from the exciting x rays is the same for both graphite and diamond and is independent of the scattering angle. It is about 284 eV, which corresponds to the K -absorption energy of carbon.

From the above features it is now certain that the spectra observed here have the following characteristics of x-ray Raman scattering predicted from the theoretical consideration above: (1) the energy shift from the exciting light is inherent to the element and coincides with the K -absorption energy, (2) the energy shift does not depend on the scattering angle, although the intensity does, and (3) the scattering spectrum reflects the local environment of the element studied; thus the two allotropes, graphite and diamond, show different spectra. Detailed features of the Raman scattering are reproducible by repeated experiments and by measurements under different experimental conditions: different excitation energies by the use of two kinds of dispersing crystals.

Equation (5) predicts that the transition moment increases with increasing scattering angle and the prediction has been qualitatively confirmed by Suzuki⁴ and Kavogli *et al.*¹³ Therefore it is favorable to employ large scattering angles to gain intensity. The Compton shift also increases with increasing the scattering angle, however, so the overlapping of the Raman spectrum with the Compton scattering becomes severe at high angles, as was already pointed out by Suzuki. Therefore, in the case of Raman scattering of carbon, 60° was chosen as the best compromise between maximizing intensity and minimizing overlapping, and the analyses described below were carried out with spectra taken at this angle.

Figure 3 shows the detailed features of (a) a raw inelastic-scattering spectrum from diamond overlapped with the Compton tail, (b) the Raman-scattering spectrum obtained by removing the Compton contribution, and (c) the oscillation extracted by assuming a smooth background as is always done in the analysis of EXAFS. In order to subtract the Compton contribution from (a), the shape of the Compton scattering was assumed to be a Lorentzian and a least-squares fitting was made. To extract the oscillation in (c), a smooth background was calculated by iteratively averaging (b) 200 times.

Figure 4 shows the soft-x-ray absorption spectrum and the extracted oscillation of diamond reproduced from Ref. 19. It is clear from comparison of Fig. 3 with Fig. 4

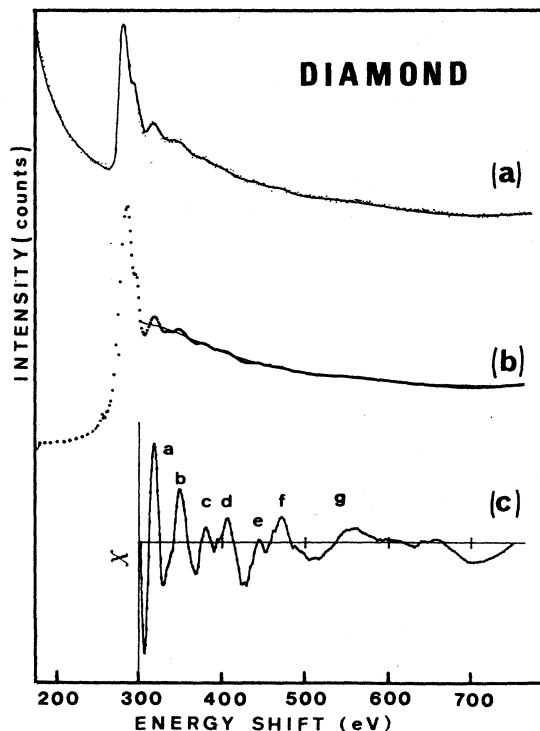


FIG. 3. (a) Part of the raw inelastic-scattering spectrum from diamond (dots) and the smoothed spectrum (solid line) observed at 60° . (b) Raman spectrum obtained from (a) by removing the Compton tail and the assumed smooth background. (c) Extracted oscillation from (b). Features (a)–(g) correspond to those in Fig. 4.

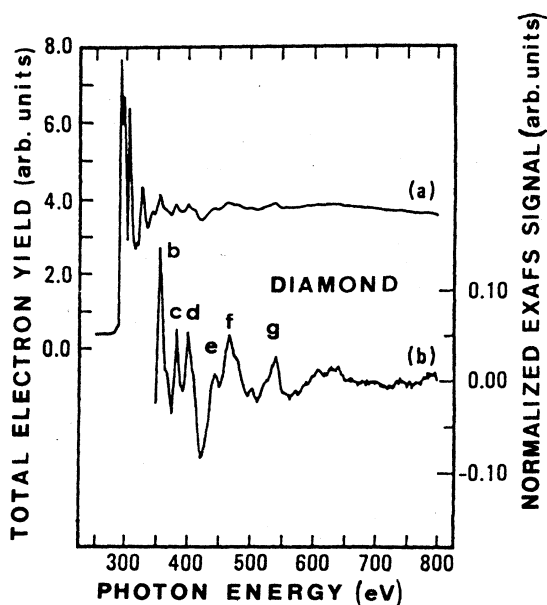


FIG. 4. (a) X-ray-absorption spectrum of diamond, and (b) the extracted oscillation reproduced with permission from Ref. 19.

that the fine structure in the x-ray Raman-scattering spectrum is essentially the same as that in the soft-x-ray absorption. For instance, the two resolved peaks observed near the edge in Fig. 4(a) appear as a distinct peak, and a shoulder in Fig. 3(a) and the third peak is well resolved in both. Except for differences due to resolution, each characteristic feature of Fig. 3(c) can be seen to have a counterpart in the EXAFS oscillation of Fig. 4(b). As far as we know, this is the first unambiguous observation that x-ray Raman scattering supplies the same spectrum as x-ray absorption.

Since the extracted oscillation from the Raman spectrum is the same as the EXAFS oscillation, Fourier transformation should give the radial structure function, which is shown in Fig. 5. Phase and amplitude parameters calculated by Teo and Lee²⁰ are taken into account and the calculation was carried out over the range $4 < k < 8.5 \text{ \AA}^{-1}$. Because the S/N ratio is not satisfactory and, consequently, the range taken for the Fourier transform is narrow, the resolution in R space is rather poor. It is still good enough to conclude that the main peak which appears at 2.52 \AA exactly corresponds to the 12 second-nearest-neighbor atoms at 2.521 \AA and that the shoulder at around 1.6 \AA indicates four nearest-neighbor atoms at 1.54 \AA in diamond. Thus, structural parameters can be obtained from the analysis of x-ray Raman scattering.

The scattering spectrum from graphite shown in Fig. 2 has been confirmed to be quite reproducible by repeated measurements on the same sample. It should be noticed, however, that, unlike diamond, a one-to-one correspondence between the features observed here and the absorption spectrum reported by Comelli *et al.*¹⁹ is absent in the case of graphite. This is not surprising at all because the spatial average leading to Eq. (3) is not adequate for oriented materials like graphite, and the effect of photon polarization and crystal direction should be properly tak-

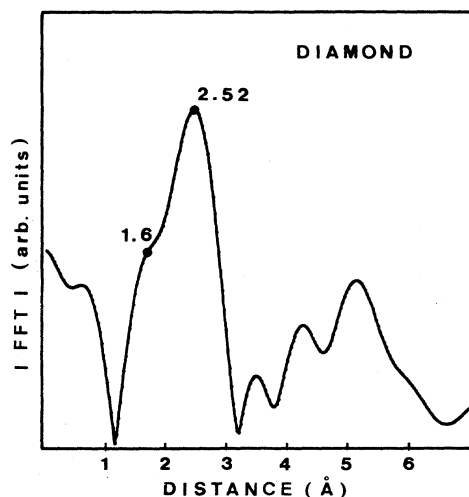


FIG. 5. Fourier transform of the extracted oscillation of diamond.

en into consideration. Indeed, Denley *et al.*²¹ observed that the x-ray-absorption spectra of several kinds of graphite from different origins are different, and attributed this difference to the orientational dependence. A polarization experiment with a perfect crystal would be required to clarify the discrepancy.

V. DISCUSSION

From the results obtained above, it is now beyond a doubt that the scattering observed here is the x-ray Raman scattering described in Sec. III. Matrix elements which originate from the A^2 term in Eq. (1) are responsible in the case of the scattering of x-ray photons by carbon. Since the equation which describes the phenomenon is, in principle, the same as that of EXAFS, x-ray Raman scattering can be utilized for the determination of local structure around a selected element in substances which do not have a long-range order, and hence it has quite wide potential applications as a substitute for EXAFS. In particular, by the use of hard x rays, light elements whose characteristic absorptions lie in the soft-x-ray region can be studied. Since the use of hard x rays makes it possible to carry out the experiment under atmospheric conditions, and since window materials such as beryllium and Kapton are available, it should be easy to investigate materials of any phase including liquid. So far, we have made preliminary experiments on carbon in polyethylene and benzene, and on boron and nitrogen in boron nitride,

and have observed the scattering spectra and confirmed that the Raman-scattering method reported here can be applied to quite a large class of materials.

A major obstacle for wide application of x-ray Raman scattering to structural determinations lies in the weak intensity of scattering. Out of 10^{11} photons impinging on the sample each second, only about 10 photons reach the detector as Raman signals. As a result, under the present experimental conditions it takes more than a day to get a spectrum with a statistical error of less than 1%. Therefore, in order for routine measurements to be possible, the x-ray-source intensity must be made much higher, or the efficiency of the spectrometer and detector must be made much better.

These difficulties will certainly be overcome in the near future by the development of insertion devices such as wigglers or undulators, which are expected to supply x rays several orders of magnitude more intense than those available at a conventional bending magnet. Then, x-ray Raman spectroscopy should become an easy task and should be widely used as a unique method for structural study.

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